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ELIMINATION OF WASHER SLIMES FROM THE PRODUCTION OF PHOSPHATE CHEMICALS

Raybon C. Cannon, et al

Florida State Department of
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ELIMINATION OF WASHER SLIMES FROM THE PRODUCTION OF PHOSPHATE CHEMICALS

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16. ABSTRACT: The report gives results of laboratory studies to determine the feasibility of a new phosphoric acid process involving dry mining of the matrix, calcination, and digestion with phosphoric/sulfuric acid mixtures (five types of Florida phosphate matrices were used). Process steps included upgrading the matrix by dry methods, calcination in a static bed, and digestion comparable to commercial dihydrate processes. The matrix samples were upgraded by removing clay by selective grinding and air classification, and by separation of the sand fraction electrostatically. Typical clay removal values were 80-90% at a phosphate loss of 15-25%. Calcination produced an acceptable phosphoric acid from good quality matrix, but failed to reject metal impurities sufficiently to permit processing of poor-to-average matrix. Calcination eliminated the interference of clay in the digestion and filtration steps. Addition of mineralizers had only marginal effect on metal solubility.

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Slime	Dry Mining	08H
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SECTION I
CONCLUSIONS

Bench-scale studies of various Florida phosphate matrix samples established that calcination at 800°C or higher eliminates the interference of clay in the digestion and filtration steps. Filtration rates of the resulting gypsum slurries were equal or better than those at present commercial plants using beneficiated phosphate rock. The acid solubilities of iron, aluminum, and magnesium minerals were reduced to 30-60% of the total, depending on the type of matrix. Although apparently all minerals containing iron, aluminum, and magnesium entered, at least in part, into the reactions forming the acid-insoluble derivatives, the metals present in clay minerals gave the best response, resulting in the highest degree of insolubilization.

The response pattern of the clay fractions to the calcination treatment was consistently different from that of the low-clay fractions. While the clay fractions exhibited a solubility minimum at 900-1000°C, the metals of the low-clay fractions became increasingly less soluble the higher the calcination temperature. For this reason, better overall metals rejection was obtained when the matrix was divided into a clay and low-clay fraction, and the fractions calcined separately at different temperatures. All types of clay investigated - montmorillonite, attapulgite, kaolin, and mixtures of the three - gave the described response pattern.

Despite the relatively good reduction in metals solubility, only one out of the five test matrix samples met the stipulated quality of phosphoric acid to be produced. Most problematic was the solubility of aluminum which responded the least to the calcination treatment but was generally present in all matrix samples at the highest concentration.

An evaluation of the calcination performance in terms of P_2O_5-to-metal ratios shows the results more clearly. Present commercial phosphoric acid production yields P_2O_5-to-metal ratios of 40, 50, and 100 for iron, aluminum and magnesium, respectively. These ratios were met by the calcination process in three out of five cases for iron and magnesium, and was approached in one for aluminum.

Attempts to improve the metals insolubilization by addition of mineralizers such as magnesium oxide, lithium fluoride, fluorspar or phosphoric oxide gave only marginal improvements. The additive concept has been reviewed in depth in Appendix C, and suggests a variety of possible approaches to insolubilizing metal impurities in phosphate matrices. However, only a few exploratory tests were conducted incidental to the primary study and the results were inconclusive, but this area probably merits further study.

Attempts to upgrade the matrix by dry methods involved selective crushing and air classification to remove a substantial amount of metal-containing minerals. However, since a certain loss of phosphate could not be avoided, the P_2O_5-to-metal ratios improved very little. Furthermore, the predominant mineral removed by this method was clay, i.e., the matrix component which responded best to the calcination treatment; thus, the overall gain in P_2O_5-to-metal ratios in the produced phosphoric acid was very small.

The proposed matrix calcination process encountered another problematic development. During the course of the investigation, the suddenly emerging energy shortage placed an unexpected economic penalty on the process. Fuel costs for calcination not only became excessive, rather fuel simply became unavailable. Fuel requirements were higher than initially anticipated because of the poor draining tendency of phosphate matrix. Most samples retain 20% moisture even after several months storage above ground. For this reason, every effort was made to reduce the mass to be calcined by separation of inert matrix components such as sand prior to the calcination. Difficulties with sand separation were encountered at USS Agri-Chemicals and at the Minnesota Minerals Research Center. However, earlier reported pilot-plant work by W. R. Grace and Company substantiated the feasibility of performing the separation by electrostatic means if the drying and clay removal is carried out simultaneously in a fluidized bed,

as described in U. S. patent 3,329,351. A similar process was recently patented to Cities Service Company, U. S. patent 3,806,046.

In summary, the calcination method was capable of producing an acceptable phosphoric acid from good quality matrix, but failed to reject metal impurities sufficiently to permit processing of poor-to-average quality matrix.

SECTION II
RECOMMENDATIONS

Since the ultimate goal set for the matrix calcination process, as outlined in Section III, was only partly met, efforts to make the process viable would have to focus predominantly on the aluminum problem, attempting the elimination by either physical separation or chemical insolubilization. A potentially improved insolubilization might be achieved by calcination in a reducing atmosphere, and/or by calcination in an agitated or fluidized bed instead of the static calcination method employed in the work of this report.

As described in Appendix C (Reference 97), carbon was found to lower the minimum temperature for mullite formation in clays. A similarly attractive effect was observed by calcining in an atmosphere of steam and/or carbon dioxide (Reference 95, 96), which also enhanced the rate of mullite formation.

The problem of acid soluble aluminum in the form of wavellite and crandallite might be resolved by addition of calcium oxide or carbonate. This reagent should displace aluminum from these minerals as the oxide and yield acid insoluble corundum. Also, increasing the calcination temperature to 1200-1300 °C might increase the acid insolubility of aluminum by improving the crystallinity of the formed compounds. However, judging from spot tests, it appears unlikely that interference of silica, forming calcium silicate, can be avoided, thus, impractical amounts of lime may be required to achieve the desired formation of corundum.

In view of the limited chances for success by presently known improvement methods and the high fuel requirements due to poor draining of the matrix, continuation of the project does not appear justified at this time.

SECTION III

INTRODUCTION

The Florida phosphate industry recovered in 1974 approximately 37 million tons of phosphate rock by strip mining and beneficiation. Of this amount, about 21 million tons were chemically converted to phosphoric acid. Both of these operations require the disposal of enormous quantities of waste by-products. The mining operation must dispose of some 32 million tons of waste clay minerals, as a dilute 3-5 percent slurry, which is allowed to settle for decades in diked settling ponds. The chemical operation produces and disposes of, as by-product, more than 23 million tons of gypsum per year in above-ground disposal sites. These disposal methods create long-term environmental effects and, in some cases, pose immediate pollution hazards to rivers and lakes.

In addition to the environmental problems, the mining and disposal methods result in considerable waste of water, mineral, and land resources. For mining and beneficiation, billions of gallons of fresh water from deep wells are required for makeup each year, with approximately 25-35 percent of the mined phosphate values discarded in the slimes. In 15 years, a plant producing 2 million tons of phosphate rock per year will require about 4,500 acres of land for slimes disposal ponds, which remain unusable without applying

expensive reclamation procedures. The gypsum by-product from phosphoric acid manufacture is not considered a potential pollutant, as are its soluble fluorine and acid contents; however, the gypsum does create an aesthetically undesirable problem by marring the land surface indefinitely.

In today's Florida phosphate strip-mining operations, the overburden is first removed and the underlying phosphatebearing matrix recovered. The matrix, actually a mixture of about equal parts of phosphate mineral, sand, and the so-called phosphate slimes containing mainly clay, is pumped as a slurry from the mine site to a beneficiation plant where it is washed, scrubbed, and beneficiated to produce an upgraded phosphate pebble and phosphate rock concentrate. During this operation, the clay and phosphate rock fines, as they are separated from the product, are collected and pumped from the washer plant as a dilute 3-5 percent by weight solids slurry to settling ponds built over mined areas. Dams reaching 35 feet in height are required to impound these slimes, since for every acre-foot of matrix, a volume of slimes equivalent to about 1.25 acre-feet is produced. A typical mineral and chemical composition of these slimes is given in Tables 1 and 2.

TABLE 1

MINERALOGICAL COMPOSITION OF PHOSPHATE SLIMES

	%
Fluorapatite	20-25
Quartz	30-35
Montmorillonite	20-25
Attapulgite	5-10
Wavellite	4- 6
Feldspar	2- 3
Heavy minerals	2- 3
Dolomite	1- 2
Miscellaneous	0- 1

TABLE 2

CHEMICAL COMPOSITION OF PHOSPHATE SLIMES

	Typical Analyses, %	Range, %
P_2O_5	9.06	9-17
SiO_2	45.68	31-46
Fe_2O_3	3.98	3- 7
Al_2O_3	8.51	6-18
CaO	14.00	14-23
MgO	1.13	1- 2
CO_2	0.80	0- 1
F	0.87	0- 1
Loss on ignition	10.60	9-16
$Ca_3(PO_4)_2$	19.88	19-37

The beneficiated phosphate rock is next converted into phosphoric acid by digestion with sulfuric acid to solubilize the phosphate values. This process also dissolves a major portion of the iron, aluminum, magnesium and fluorine associated with the phosphate. The phosphoric acid and gypsum are then separated by filtration. Soluble fluorides and phosphates contained in the wet gypsum cake are dissolved in the pond waters. Figure 1 schematically outlines the basic operations from mine to phosphoric acid which are required to produce merchant-grade phosphate values by conventional methods.

For three major reasons, the matrix, which of course includes the slimes, cannot be directly used as feed to digestion. First, the impurity content of the matrix, particularly iron, aluminum, and magnesium is considerably higher than in beneficiated phosphate rock, and it is largely solubilized by sulfuric acid. Phosphoric acid of unacceptable quality results. Secondly, if the clays are not removed from the matrix before digestion, a much more dilute phosphoric acid must be produced to overcome the thickening effect of the clays on the digestion slurry. Thirdly, the presence of colloidal clays makes filtration of the gypsum economically unacceptable due to blinding of filters and extremely slow filtration rates.

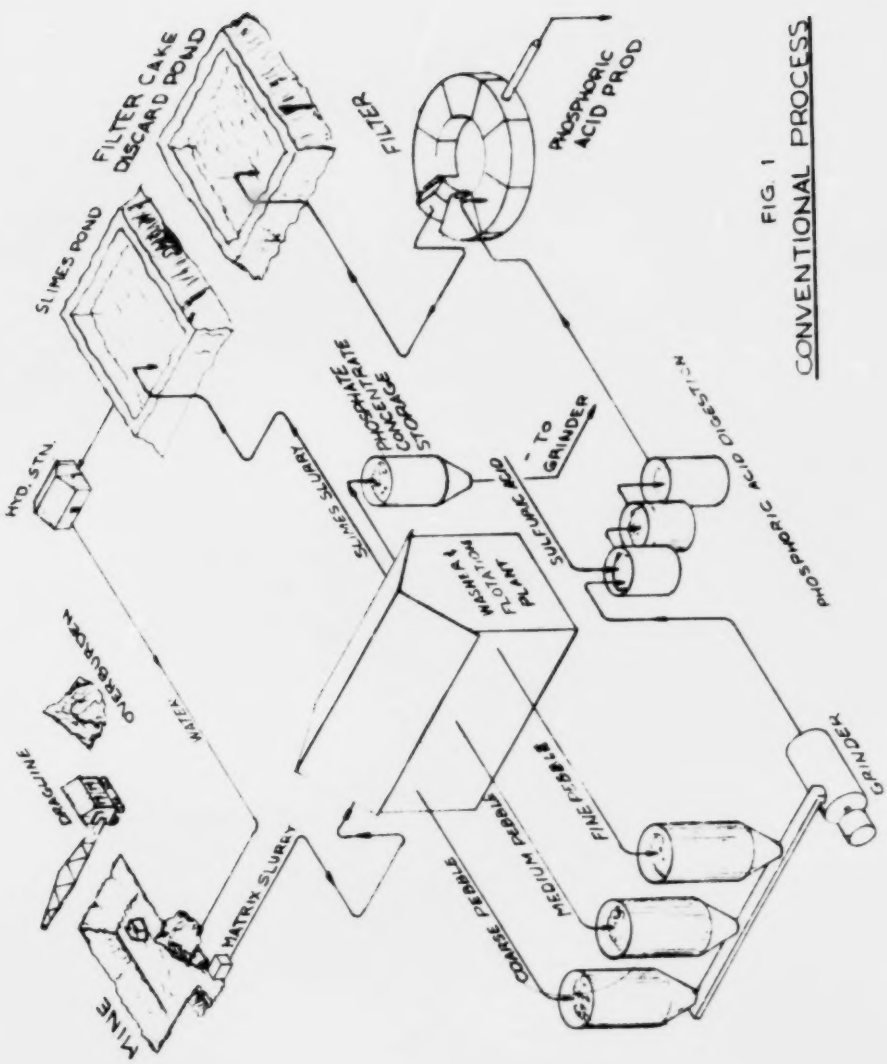


FIG. 1
CONVENTIONAL PROCESS

This project was initiated because it became apparent that after-the-fact methods would not result in complete solutions to industry waste disposal problems. New concepts and techniques are necessary to meet domestic needs and the environmental control required to continue and extend the life of the Florida phosphate industry. The waste disposal problems of the industry are detailed below to emphasize the magnitude and the necessity of finding solutions to these problems.

The techniques used in the recovery of Florida phosphate have not changed in basic concept for the last 20 years. Despite the many suggested new methods for slimes disposal, none have been economically attractive. Several proposals have involved manufacture of products, such as lightweight aggregate, tile, etc., from slimes, and wallboard from gypsum. Products from these materials are at best marginally economical in a few cases, and the market volumes can by no means be projected to result in an industry-wide solution to the problems. The proposal of the matrix calcination process was based on the concept that new technology needs to be developed which would eliminate slimes formation in the first place, and which would better utilize available resources, thereby contributing to the establishment of a more acceptable economic situation to encourage change.

The techniques used by the Florida phosphate industry so far have the following disadvantages from the standpoint of water and mineral conservation, environmental hazard, and land usage:

1. Large volumes of water are required for mining and beneficiation, with makeup requirements of some 80 billion gallons per year,

2. approximately 15 million tons of phosphate values are discarded as waste each year,

3. the present slimes disposal systems tie up land resources indefinitely; for example, at the present production rate of 37 million tons per year, about 82,000 acres of slimes ponds are required for 15 years operation,

4. retaining dams around each 50-400-acre slimes disposal pond require continual maintenance and checking, with the ever present possibility of dam breakage and resultant river, lake, and stream pollution,

5. annual above-ground disposal of some 23 million tons of gypsum by-product per year is aesthetically unattractive and becomes a permanent feature of the topography, and

6. tne soluble acid content, and particularly the soluble fluorine content, of the gypsum disposal ponds and piles are potential hazards since they may enter the environment by leaching and run-off during heavy rainfall, by seepage, and by evaporation from the surface of the ponds.

Consequently, a dry-mining calcination-digestion concept was developed, based on the laboratory observation that calcination of phosphate matrix to certain temperatures eliminates the interference of clay in the phosphoric acid process and simultaneously decreases the acid solubility of most metal impurities. The original concept involved a total of five steps:

1. Dry mining of the matrix,
2. upgrading by dry methods,
3. calcination,
4. digestion to produce phosphoric acid, and
5. return of gypsum and acid insoluble by-products to the mining pits.

Successful completion of all phases of this concept would result in a new process with the following benefits:

1. Closed-loop operation where all of the major mining and chemical plant by-products would be disposed of in mine pits without above-ground-level dikes and ponds,
2. the utilization of at least 90 percent of the actually mined phosphate values,
3. a major reduction in the deep-well water makeup requirements, and

4. complete elimination of slimes pond environmental hazard and potential fluorine runoff, leaching, and evaporation from gypsum ponds.

A literature search of publications relating to the postulated reactions of the matrix calcination was initiated to establish prior art before the beginning of extensive laboratory work and to aid in planning of the experimental phase. The search covered Chemical Abstracts Volumes 41-77 (1947-1972). It is presented as Appendix C. Only a few references were found which deal directly with the chemical nature of acid-insoluble iron, aluminum, or magnesium compounds formed by calcination.

SECTION IV

MATRIX CHARACTERIZATION

A total of five phosphate matrix samples were evaluated in the course of studying the matrix calcination-digestion process. The samples were selected to represent all major types of typical Florida matrix, and were taken directly from mining sites of five major mining companies in Florida as indicated in Figure 2. Preparation of the samples for process studies involved air drying to 0.5-3% moisture, crushing with a jaw crusher to 3/16 in., and blending in a 55-gal drum tumbler. The stainless-steel drum used for the blending was equipped with baffles to avoid rolling of the charge. Subsamples were withdrawn while the drum was in motion. A test for representativeness as shown in Table 3 confirmed the efficiency of the blending equipment.

TABLE 3

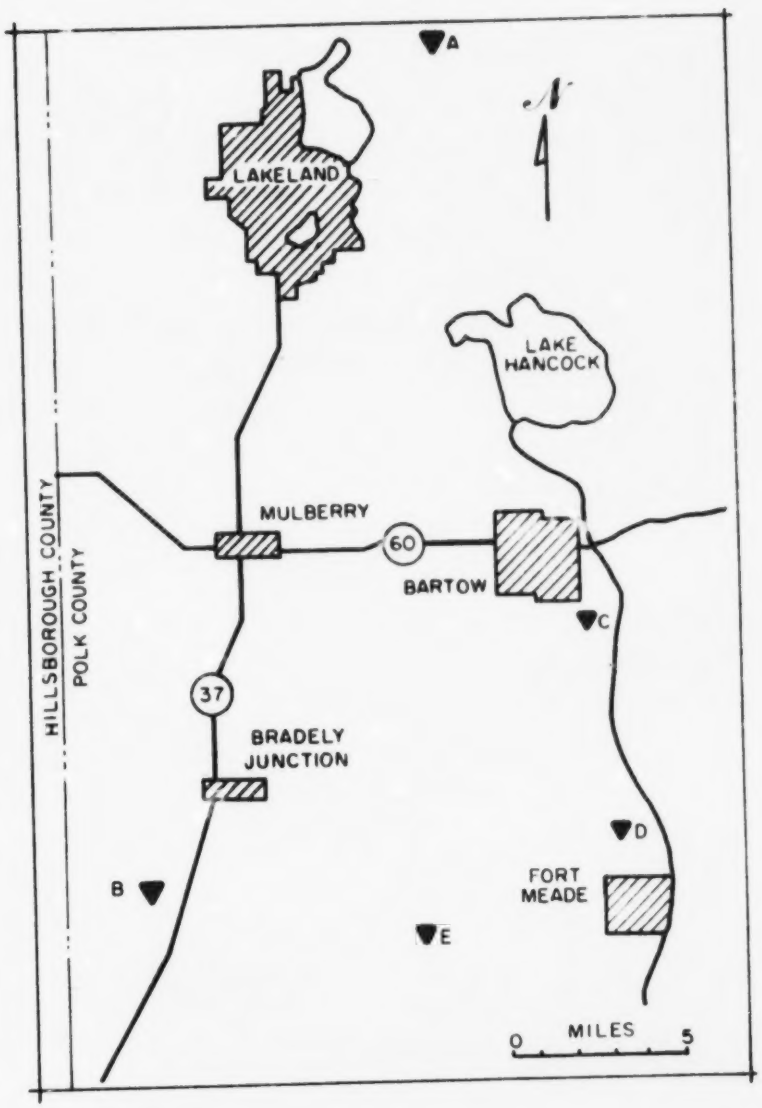
STUDY OF SAMPLING REPRESENTATIVENESS

Ref. No.	Blending Time, min	%				
		P_2O_5	Fe	Al	Mg	H_2O
320-15-1	30	9.70	1.11	1.78	0.38	2.77
320-15-2	30	9.68	1.10	1.71	0.33	2.84
320-15-3	60	9.81	0.96	1.62	0.33	2.68
320-15-4	60	9.79	1.12	1.63	0.33	2.62

In this test, four 20-lb samples were withdrawn, two each after 30 and 60 minutes of blending, respectively. Each sample was analyzed after riffling and grinding to -100 mesh (Tyler). Chemical compositions of

FIGURE 2

MATRIX SAMPLE LOCATIONS



A. BORDEN
B. AM. CYANAMID
C. IMC
D. MOBIL
E. USSAC

all matrix samples are listed in Table 4. A typical particle size distribution of the crushed or ground matrix is presented in Table 5.

TABLE 5

PARTICLE SIZE DISTRIBUTION
USSAC MATRIX

Ground Matrix		Crushed Matrix	
Screen Analysis (Tyler)	%	Screen Analysis (Tyler)	%
+60	0.24	+3	1.86
-60+100	16.65	-3+4	0.40
-100+200	29.13	-4+8	0.59
-200	53.98	-8+10	0.40
		-10+16	1.19
		-16+28	24.73
		-28+60	19.71
		-60+100	25.52
		-100+200	11.87
		-200	13.73

The mineralogical compositions of the matrix samples were determined by X-ray diffraction [1,2] and microscopic examination. Separation into various mineral fractions for the purpose of identification was performed by classification according to differences in hardness, gravity, acid solubility, and streak. A comparison of major mineralogical characteristics of all matrix samples is listed in Table 6. The terminology of data in this table follows the customary practice of the phosphate mining industry designating the -150 mesh fraction as slimes, the -14+150 mesh fraction as flotation feed, and the +14 mesh fraction as pebble.

TABLE 4

CHEMICAL COMPOSITION OF MATRIX SAMPLES

	USSAC	Borden	American Cyanamid	IMC	Mobil
P_2O_5	9.67	20.09	15.70	12.27	15.72
Acid insol.	63.87	39.87	51.80	58.43	51.76
CaO	13.41	29.40	21.33	14.98	21.66
SO_4	0.34	0.67	0.57	0.85	0.90
Org. Matter	0.15	0.19	0.19	0.15	0.27
F	1.19	2.13	1.48	1.00	1.84
CO_2	0.30	-	-	-	-
Fe	1.18	0.419	0.517	0.79	1.84
Al	2.23	1.17	1.32	3.05	1.32
Mg	0.40	0.125	0.157	0.144	0.153
Na	0.21	-	-	-	-
K	0.72	NF	NF	NF	NF
Moisture	-	0.53	0.58	0.57	0.45
P_2O_5/Fe, wt. Ratio	8.2	48.0	30.4	15.6	8.6
P_2O_5/Al, wt. Ratio	4.3	17.2	11.9	4.0	11.9
P_2O_5/Mg, wt. Ratio	24.2	160.7	109.0	85.2	102.7

TABLE 6

MINERALOGICAL CHARACTERISTICS OF MATRIX SAMPLES

Matrix Source	Clay[1]		% in Matrix				Pebble[4]
	Type	%	Slimes[2]	P_2O_5	Pebble	Feed[3]	% weathered
USSAC	Montmorillonite	27.4	33.0	9.7	0	52.2	no pebble
Borden	Kaolin	2.2	8.8	20.4	4.5	87.7	nil
American Cyanamid	Montmorillonite Kaolin Attapulgite	7.3	17.5	18.9	39.5	43.0	25
IMC	Montmorillonite	-	35.7	12.1	2.9	61.5	75
Mobil	Attapulgite	23.4	69.3	6.9	1.1	29.6	nil

[1] Clay = -1µ

[2] Slimes = +1µ -150 mesh

[3] Feed = -14+150 mesh material

[4] Pebble = +14 mesh material

The main purpose of evaluating several matrix samples was to establish the response of different matrix types and components to the calcination treatment. As evident from Table 6, the matrix samples contained montmorillonite, attapulgite or kaolin clay, or a mixture of all three. Further differences were the presence of weathered and unweathered pebble, as well as one case of iron in solid solution in the pebble. The distribution of P_2O_5 and metals is listed in Table 7. Detailed results of the matrix characterization are as follows.

USS Matrix, Rockland Mine

The USSAC sample was a high quartzite, high aluminum matrix with very little pebble phosphate. Its clay content was about average for a Florida matrix, being nearly all montmorillonite. There was a substantial amount of aluminum in minerals other than clay. Listed in decreasing order of occurrance, the following components were found:

Quartz	Apophyilite	
Apatite	Illmenite	
Montmorillonite	Wavellite	
Staurolite	Rutile	Traces
Feldspar	Illite	

Borden Matrix, Tenerock Mine

The sample is representative of the older mining operations in the northern section of the Florida phosphate field. Because of its high phosphate content, this area has been mined very intensively. Its clay content was mainly kaolin. The sample contained an above average amount (87%) of -14+150 mesh material which normally is used as flotation feed. Its sand fraction was very fine, usually -40 mesh.

TABLE 7

PARTICLE SIZE, P_2O_5 AND METALS DISTRIBUTION IN MATRIX SAMPLES

(ATC 320-39)

	Wt. %	% P_2O_5	% P_2O_5 Distr.	% Al	% Al Distr.	% Fe	% Fe Distr.	% Mg	% Mg Distr.
Borden									
Pebble	4.5	33.5	7.4	0.56	2.1	0.43	4.9	0.125	4.8
Feed	86.7	20.6	87.5	0.54	38.4	0.26	58.0	0.085	64.9
+1μ Slimes	6.6	13.0	4.2	7.85	42.4	1.54	25.9	0.375	21.8
-1μ Slimes	2.2	9.2	0.9	9.52	17.1	2.00	11.2	0.446	8.5
American Cyanamid									
Pebble	39.45	31.4	65.5	0.71	19.5	0.59	45.9	0.168	32.8
Feed	43.01	6.6	15.0	0.25	7.5	0.19	15.9	0.050	10.6
+1μ Slimes	10.29	21.6	11.7	5.91	42.2	0.98	19.8	0.497	25.3
-1μ Slimes	7.25	20.3	7.8	6.12	30.8	1.29	18.4	0.879	31.3
IMC									
Pebble	2.85	32.0	7.5	0.33	0.8	0.48	1.9	0.088	1.8
Feed	61.50	8.3	42.3	0.54	10.0	0.21	17.4	0.035	15.5
Slimes	35.65	17.1	50.2	8.33	89.2	1.85	80.7	0.322	82.7
Mobil									
Pebble	1.09	18.4	2.9	0.59	0.3	0.53	0.4	0.626	0.9
Feed	29.62	13.8	59.4	0.73	10.3	0.39	7.3	0.300	12.2
+1μ Slimes	45.32	5.0	33.3	3.41	74.5	1.38	54.7	0.777	48.8
-1μ Slimes	23.97	1.3	4.4	1.34	14.9	2.04	37.6	1.190	38.1

American Cyanamid Matrix, Haynsworth Mine

The sample from American Cyanamid originated from the southwestern location of the phosphate field and represented the newer mining areas toward Manatee County.

This matrix had a more typical distribution of apatite, sand, and clay. It had a high pebble content, which contained an iron impurity in solid solution. The sand fraction was present in rather coarse form. Most of the clay was a mixture of montmorillonite, attapulgite, and kaolin.

IMC Matrix, Clear Springs Mine

The matrix from IMC was quite similar to the USSAC sample, except for weathering. The Clear Springs Mine is located in the lateritic weathering belt, and consequently about half of the pebble showed strong weathering. Similar to the USSAC matrix, the clay fraction consisted almost exclusively of montmorillonite, and constituted about one-third of the matrix. The sand fraction contained both coarse and fine sand.

Mobil Matrix, Ft. Meade

Mobil's mine is located near the southeastern end of the lateritic weathering belt. The weathering is mainly evident in the flotation feed fraction. Since the sample contained 70% clay, it cannot be considered a representative matrix sample. The Mobil matrix was evaluated mainly because it contained primarily attapulgite clay and therefore gave an indication of the calcination performance of attapulgite.

SECTION V

MATRIX UPGRADING METHODS

Any removal of nonphosphate matrix components prior to the calcination step improves the process economics by reducing fuel requirements. In the case of clay removal, an additional benefit of eliminating some of the iron and aluminum can also be realized. Preparatory measures to apply any upgrading treatment included drying of the matrix to less than 3% moisture and crushing to 3/16 in.

CLAY SEPARATION

The removal of clay from the predried matrix was most efficiently accomplanished by air classification. This method floats the lighter clay particles from the phosphate and sand fractions of the matrix. Consequently, the preparatory treatment such as drying and particle size reduction is very crucial for the success of the operation.

The apparatus used for the air classification study consisted of a cylindrical fluidization chamber (4x24 in.) supplied with 40-50 ft^3/min of air through a perforated disc at the bottom. The temperature of the air was controlled by an electric heater.

Unground matrix was treated in 14 runs. Only 15 minutes were required per run to remove all fines from the samples. However, the clay removal did not exceed 24% of the total clay present in the sample.

Grinding of the matrix improved the clay removal substantially, but the run time during air classification had to be doubled to remove all fines. Chemical compositions of the air-classified clay fractions are listed in Table 8.

TABLE 8

CHEMICAL COMPOSITION OF CLAY FRACTIONS

(ATC 320-23)

	Concentration, %				Clay
	P_2O_5	Fe	Al	Mg	Removal, %
Clay, Unground Matrix	7.18	1.24	5.26	0.99	24
Clay, Ground Matrix	10.32	1.14	4.90	0.77	96
Matrix Sample	9.67	1.19	2.25	0.40	-

The particle size reduction was tested with an impactor (6-in. hammer mill without screens) at 2000 and 4000 rpm and with a ball mill (6x8 in.) charged with ceramic cylinders, operated at 65 rpm, which approached critical speed. Results are tabulated in Tables 9 and 10 (Appendix A). Loading variation of the ball mill had little effect on the grinding and air classification performance as evident from data of Table 11 (Appendix A). A comparison of impactor versus ball mill grinding is listed in Table 12 (Appendix A).

A third variation was tested by use of a 24-inch drum tumbler. It was operated without load (balls or cylinders) at the same percent of critical speed as the ceramics ball mill. Three runs of 45 minutes each, followed by the standard air classification treatment, achieved approximately 68% removal of the dust fraction (-150 mesh).

SAND SEPARATION

Samples for studies of sand separation by electrostatic means were predried to approximately 10% moisture, crushed in an impactor at 2000 rpm, and dried to 0.5-3% moisture in a fluidized bed at 65°C. Each sample was then given a two-stage light grind in the ball mill followed by dedusting in a fluidized bed to remove 80-90% of the dust fraction (-150 mesh).

All experiments were carried out with a UNIVERSAL ELECTROSTATIC SEPARATOR Model 1700. Test conditions and results are listed in Tables 13 and 14 (Appendix A). In the operation of the electrostatic separation, the middling and tail fractions were passed through the separator three times. A concentrate fraction was collected on each pass, and the three concentrates combined. The water-washed matrix samples were run for comparison purposes.

Additional electrostatic separation tests were performed at the Mineral Resources Research Center of the University of Minnesota. A free-fall separator was used consisting of a pair of parallel plate electrodes, one foot wide and three feet long, separated by 7 in., with a potential difference of 60,000 volts.

For all tests, the sample to be tested was held in an oven until it reached 105°C. It was delivered by a SYNTRON feeder and passed through a plastic chute mounted midway between the electrodes at a

rate of about 0.2 ton per hour distributed over the one-foot width of the electrodes. The products were collected in a series of one-inch-wide product pans numbered from 1 (negative electrode) to 12 (positive electrode). The pans were positioned 5 inches below the lower edge of the electrodes, with the divider between pans 6 and 7 midway between the two electrodes. After examining the products of the first three tests, the samples were grouped in the following manner:

Phosphate Concentrate	:	Pan 1-3
Middling 1	:	Pan 4-5
Middling 2	:	Pan 6-8
Quartz Tailing	:	Pan 9-12

Analytical results and percent metals distribution of the Minnesota tests are reported in Table 15 (Appendix A). The only variable in the four tests was the method of scrubbing. In test A the sample was used as received, in test B the sample was jigged over a screen, in test C it was subjected to shear scrubbing, and in test E to attrition scrubbing.

SECTION VI

CALCINATION AND DIGESTION STUDIES

Matrix samples for the calcination and digestion study were obtained by withdrawing a 10-kg portion of the predried stock matrix from a drum blender while rotating. After riffling into two 5-kg samples, one portion was ground to -100 mesh and the other subdivided into 200 to 300-g portions by additional riffling.

CALCINATION PROCEDURE

All calcinations were carried out in a THERMOLYNE furnace, Model F-A1520M. The charge temperature was measured by a thermocouple immersed in the sample, which indicated a temperature constance of $\pm$ 5°C, as monitored by a continuous recorder.

In the standard procedure for calcination of matrix, approximately 150-200 g of the sample was placed in the preheated furnace in a Vycor dish. Warmup of the sample to the specified temperature required 20-30 minutes. The listed calcination times do not include this warm-up period. After completion of heating, the sample was removed from the hot furnace, allowed to cool to ambient temperature, ground if necessary, and screened before the subsequent digestion in acid.

DIGESTION PROCEDURE

The digestion of the calcined matrix with sulfuric acid was performed in a 1-liter cylindrical polypropylene reactor equipped with four vertical 3/8-in. baffles, spaced equally around the wall. Agitation

was provided by a stainless-steel stirrer with a blade length of three-fourths of the reactor diameter. The rate of agitation was adjusted to the minimum required to keep the solids suspended. A lid with appropriate cutouts for the stirrer shaft, and for the rock and acid additions was installed to minimize evaporation. Control of temperature was achieved by a thermostat-regulated water bath in which the reactor was immersed.

In a typical digestion experiment, a pool of 30% P_2O_5 chemically pure phosphoric acid (150 g) was heated in the reactor to 75-85°C. Matrix (150-200 g) and hot (75°C) sulfuric acid (25% H_2SO_4) were added continuously over a period of approximately 60 minutes. Every 10 minutes a 2-ml sample was withdrawn to determine free sulfuric acid concentration. Lengthening or shortening of the reactant addition time decreased or increased the free sulfuric acid in the reactor slurry. After all reactants were added, the digestion mixture was cured for 15 or 60 minutes while maintaining temperature and agitation. Water was added very slowly to compensate for loss by evaporation. The hot slurry was then filtered through a polypropylene test leaf of 0.1 ft^2 filter area and washed with three 100-ml portions of water. Filtration rates were determined at 15 in. vacuum.

Major process parameters for the combined calcination-digestion study were established in a preliminary screening experiment where a total of seven variables where evaluated for their dominance in the over-all process. Each variable was tested at two levels as shown below.

	Variable	Level	
Calcination	1. Temperature, °C	980	1095
	2. Time, minute	20	60
	3. Particle Size, mesh	-100	-6
Digestion	4. Temperature, °C	65	85
	5. Cure Time, minute	15	60
	6. Acid Strength, % SO_4	1.5	4.0
	7. Particle Size, mesh	-100	-20

These variables were studied at two levels according to a fractional factorial design using a one-eighth replicate of the 2^7 factorial[3]. The design required sixteen experiments, which were run with the USSAC matrix using the previously described standard calcination and digestion procedures.

Experimental conditions and results of the study are listed in Table 16. Table 17 shows the same results expressed on a P_2O_5-to-metals ratio basis. As evident from the data, the main variables of the process were calcination temperature, particle size in calcination and digestion, and acid strength in digestion. This conclusion was based on statistical evaluation (t-Test) of the experimental data. Table 18 summarizes the response of the P_2O_5 and metal solubilities according to the specific variables. The numbers in parentheses, giving the statistical confidence level, indicate whether respective pairs of averages are truly different.

Subsequent work in the calcination-digestion study was carried out over a temperature range of 700-1100°C, at a fixed particle size of -100 mesh for both calcination and digestion, and at an acid strength of 2.5% SO_4 during digestion.

TABLE 16

CONDITIONS OF CALCINATION - DIGESTION STUDY

(ATC 324-10-1)

Experiment Number	Experimental Conditions						
	Calcination			Digestion			
	Particle Size, Mesh	Time, Min	Temp., °C	Particle Size, Mesh	Sulfate %	Temp., °C	Cure Time, Min
1	-6	20	1095	-100	4.0	65	15
2	-6	60	980	-100	1.5	65	60
3	-100	20	1095	-100	1.5	85	60
4	-6	20	980	-100	4.0	85	60
5	-6	60	1095	-100	1.5	85	15
6	-100	60	1095	-20	1.5	65	15
7	-100	20	1095	-20	4.0	85	15
8	-100	20	980	-20	4.0	65	60
9	-100	60	1095	-100	4.0	65	60
10	-100	60	980	-20	1.5	85	60
11	-100	20	980	-100	1.5	65	15
12	-6	20	980	-20	1.5	85	15
13	-100	60	980	-100	4.0	85	15
14	-6	60	1095	-20	4.0	85	60
15	-6	20	1095	-20	1.5	65	60
16	-6	60	980	-20	4.0	65	15

TABLE 17

RESULTS OF CALCINATION - DIGESTION STUDY

(ATC 324-10-1)

Experiment Number	Extraction Performance, % of Total				Weight Ratio Extracted		
	P_2O_5	Fe	Al	Mg	P_2O_5/Fe	P_2O_5/Al	P_2O_5/Mg
1	94.6	20.0	42.7	41.4	37.9	9.5	48.6
2	95.9	46.4	32.2	41.1	28.7	12.8	92.8
3	93.1	38.8	57.0	51.8	19.6	7.0	43.7
4	87.2	42.6	36.1	39.3	16.7	10.4	53.1
5	97.2	25.2	44.4	45.5	31.3	9.4	51.5
6	78.0	12.1	43.9	57.1	53.5	7.6	32.9
7	73.7	16.3	41.4	45.5	36.7	7.7	39.1
8	76.9	18.7	36.1	30.0	33.3	9.2	55.0
9	89.9	18.0	58.5	47.7	41.1	6.6	39.9
10	85.5	24.6	40.2	32.5	28.1	9.1	52.1
11	78.6	25.3	36.7	28.9	25.4	9.2	58.8
12	79.3	13.1	20.1	16.4	48.3	16.9	100.2
13	76.2	22.8	37.2	33.9	27.2	8.8	54.5
14	51.0	13.5	38.6	26.6	31.1	5.7	39.9
15	44.2	15.5	38.5	26.6	26.7	4.9	34.6
16	32.4	7.3	23.9	16.4	35.5	5.8	40.9

TABLE 18

SUMMARY OF VARIABLE RESPONSE[1]

	Average Extraction, % of Total			
	P_2O_5	Fe	Al	Mg
Particle Size:				
-6 mesh	72.7 (80)	23.0 (55)	34.6 (97.5)	31.7 (93)
-100	81.5	22.1	43.9	40.9
Calcination Time:				
20 min.	78.5 (60)	23.8 (65)	38.6 (60)	35.0 (65)
60 min.	75.8	21.2	40.0	37.6
Calcination Temperature:				
980°C	76.5 (55)	25.1 (80)	32.8 (99.5)	29.8 (98)
1100°C	77.7	19.9	45.6	42.8
Digestion Particle Size:				
-20 mesh	65.1 (99.5)	15.1 (99.5)	35.3 (94)	31.4 (95)
-100 mesh	89.1	29.9	43.1	41.2
Sulfate Concentration:				
1.5%	81.5 (85)	25.1 (85)	39.1 -	37.5 (65)
4.0%	72.7	19.9	39.3	41.2
Digestion Temperature				
65°C	73.8 (70)	20.4 (78)	39.1 -	36.2 -
85°C	80.4	24.6	39.4	36.4
Cure Time:				
15 min.	76.3 (55)	17.8 (95)	36.3 (88)	35.6 (55)
60 min.	78.0	27.3	42.2	36.9

[1] Averages listed for each category are statistically equal unless the confidence level is 90% or greater. Statistical confidence limits are shown in parentheses.

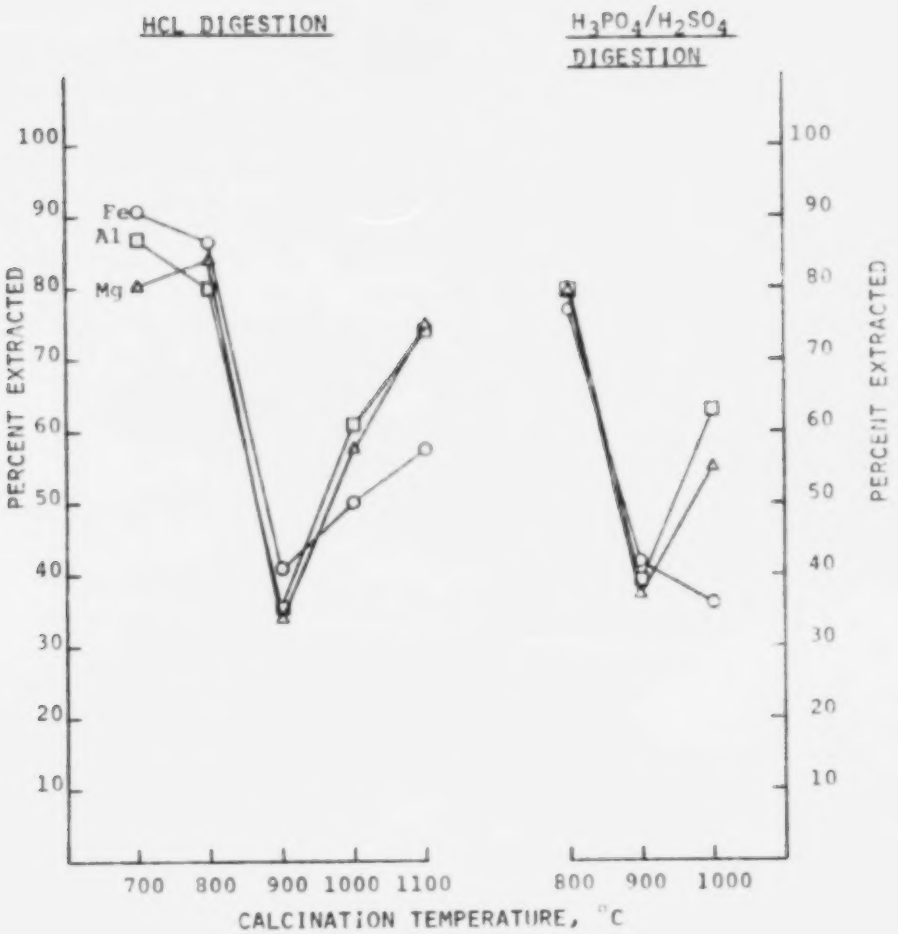
Most matrix samples and matrix components were checked by differential thermal analysis (DTA) for specific temperatures at which reactions or phase transformations took place. A DELTATHERM Model 2000 was used for all DTA work. Results are summarized in Table 19 (Appendix A).

All calcination samples were prescreened for P_2O_5 and metals solubilities by a hydrochloric acid digestion to establish the general trend of solubility response. An oxidizer such as hydrogen peroxide or nitric acid was added to facilitate the digestion. Areas of specific interest were then evaluated in detail by the more time-consuming but more representative phosphoric-sulfuric acid method described above. Both methods indicated the relative response of the solubilities to the calcination treatment, as shown in Figure 3, and therefore were useful to interpret data. However, only the phosphoric-sulfuric acid digestion is representative on an absolute level, which is required for yield predictions, etc.

Initial calcination tests (Figures 4 and 5) scanning the full temperature range from 700 to 1200°C established that the low-clay fraction (+150 mesh) of the matrix responded differently in the calcination treatment as compared to the clay fraction (-150 mesh). Also, sintering occured at temperatures above 1100°C. Consequently, all subsequent studies were carried out with the matrix separated into low-clay and clay fractions as well as with the total matrix, and the temperature was limited to 1100°C. Results of these calcination experiments are summarized

FIGURE 3

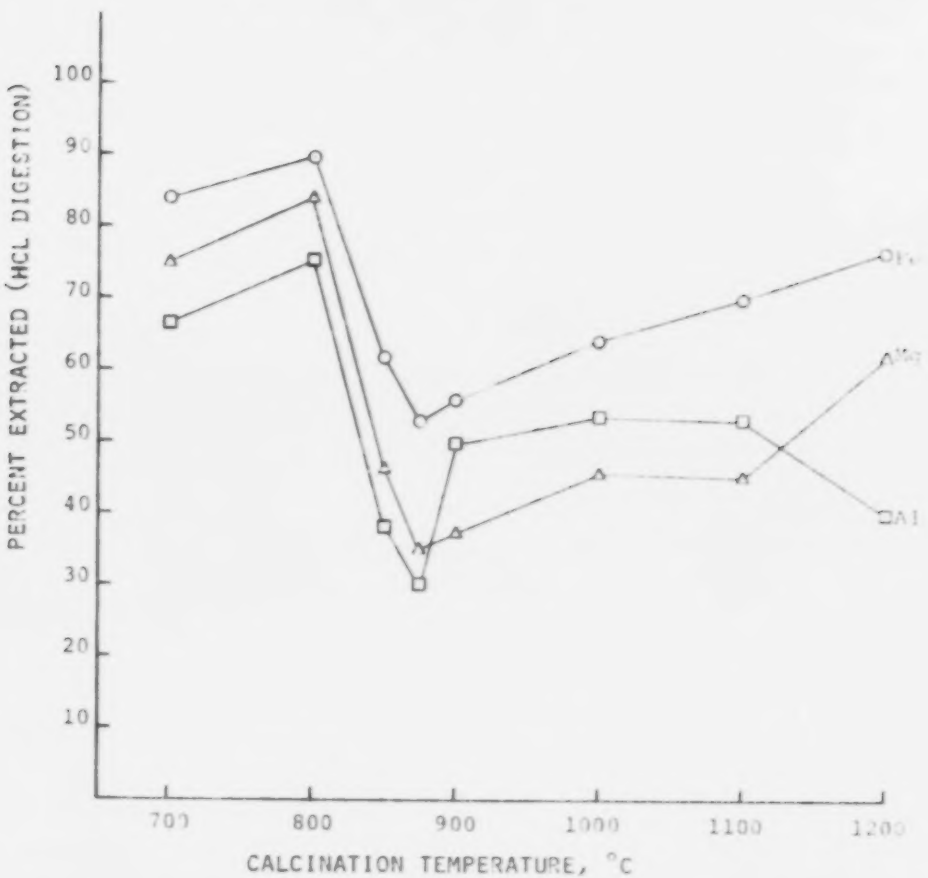
COMPARISON OF DIGESTION METHODS



ATC 324-42

FIGURE 4

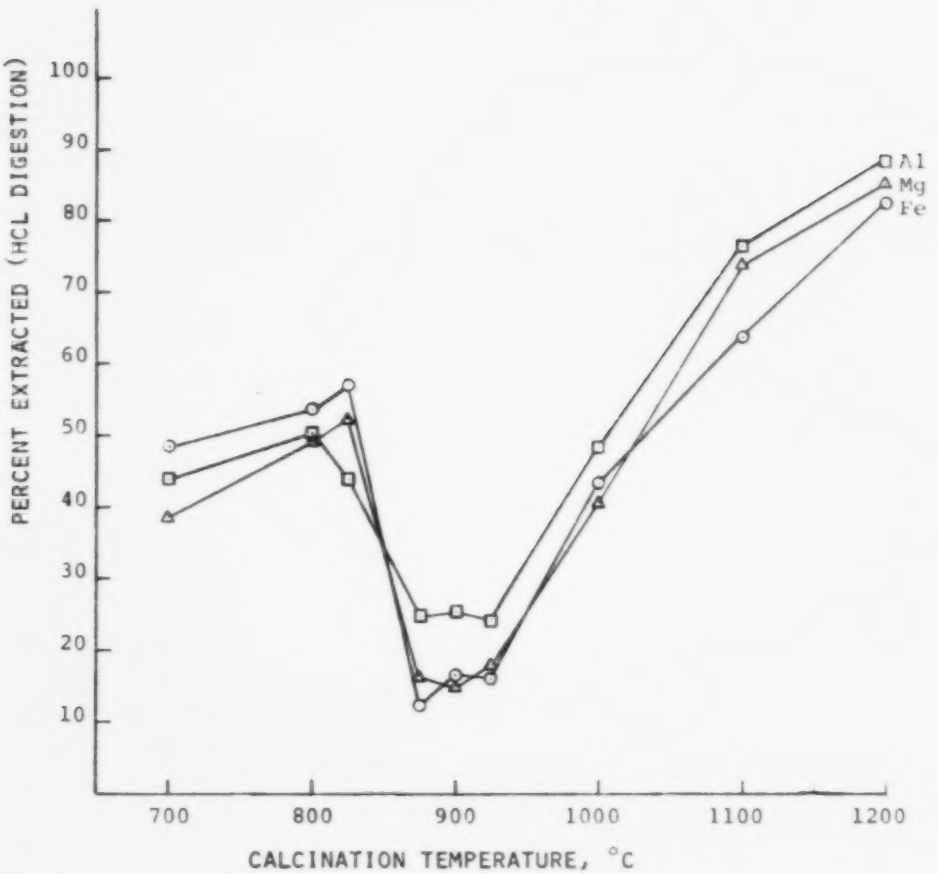
METALS SOLUBILITY OF
LOW-CLAY FRACTION



NTC 322-42

FIGURE 5

METAL SOLUBILITY OF
OF CLAY FRACTION



ATC 321-26

graphically in Figures 6-10 (Appendix B), using the hydrochloric acid digestion method. Figures 11-15 (Appendix B) show the same experiments evaluated by the phosphoric-sulfuric acid method.

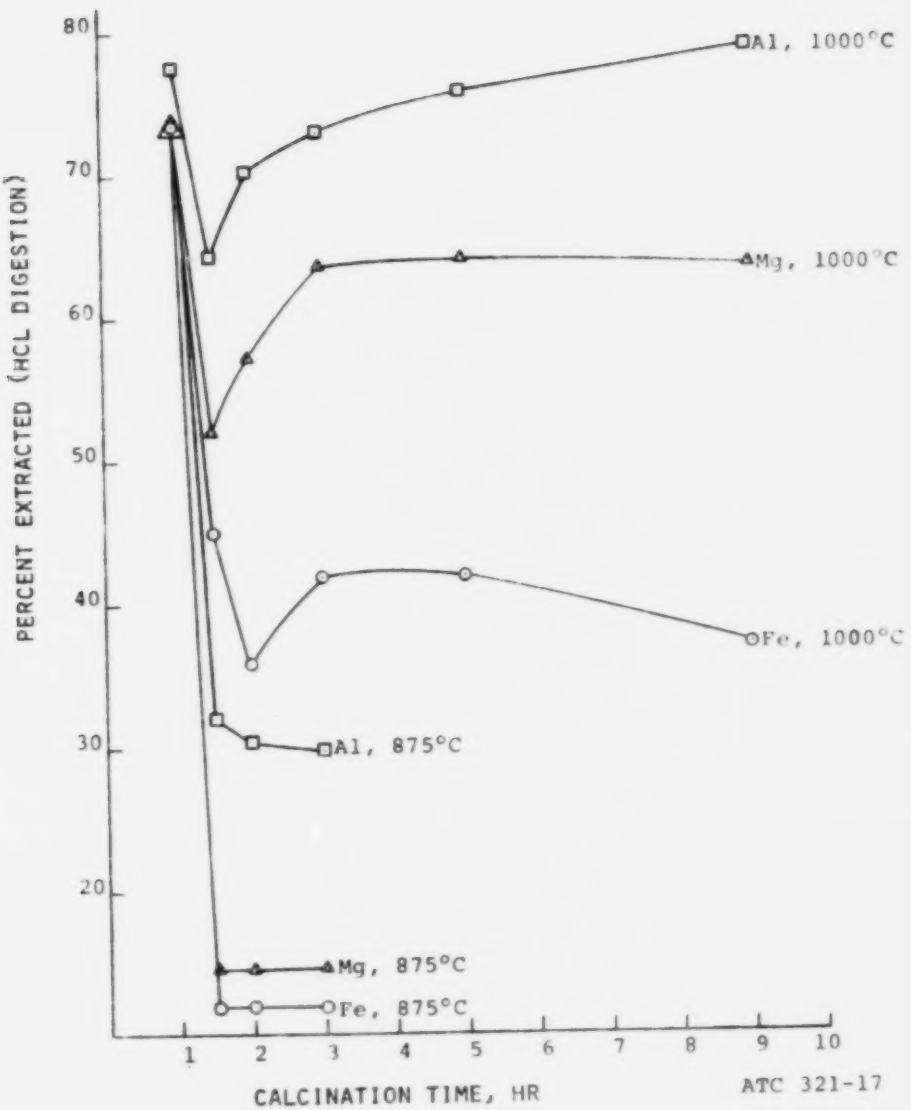
A detailed evaluation of the time effect of the calcination on the clay fraction (USSAC) covering a range of 0.5 to 8 hours is presented in Figure 16. A similar, though less detailed, study was made with the clay fraction where the final calcination temperature was approched stepwise. This test is reported in Table 20 (Appendix A).

Comparable studies with the complete matrix (USSAC) were performed to confirm the applicability of the results from the clay fraction to the total matrix. The results are listed in Table 21 (Appendix A). In each experiment, the matrix was heated in a porcelain crucible to the indicated temperature at a rate of 10°C per minute. Cooling to ambient proceeded at 3°C per minute.

Several calcination tests were performed with the addition of so-called mineralizers which are cited in the literature to either promote solid state reactions or to lower the minimum temperature at which these reactions proceed. The additives tested in this study were magnesium oxide, lithium fluoride, fluorspar (calcium fluoride), and phosphoric oxide. These additives were premixed with the test samples in a pulverizer prior to calcination at the indicated concentration. After calcination, metals solubilities were determined by the hydrochloric

FIGURE 16

EFFECT OF CALCINATION TIME ON
METALS SOLUBILITY OF CLAY FRACTION



acid method. The results in Table 22 include, in the case of phosphoric oxide addition, the added phosphate in the P_2O_5 column. However, the P_2O_5-to-metal ratios were calculated excluding the added phosphate.

TABLE 22

CALCINATION OF CLAY FRACTION AT 1000°C WITH MINERALIZERS

(ATC 321-20)

Calcination Time, hr	Mineralizer, Wt. %	% Extraction(HCl Digestion)				P_2O_5/Metal Weight Ratio		
		P_2O_5	Al	Fe	Mg	Al	Fe	Mg
2	none	-	73.0	41.9	63.7	1.8	7.0	11.0
1	3.8% MgO	94.1	67.6	41.9	77.9[1]	2.0	7.2	2.7[1]
2	3.8% MgO	-	64.4	36.9	72.9[1]	2.0	8.1	2.8[1]
4	3.8% MgO	-	66.8	38.8	72.9[1]	2.0	7.7	2.8[1]
8	3.8% MgO	93.9	67.2	36.6	71.7[1]	2.0	8.1	2.9[1]
2	0.5% LiF	-	77.8	55.6	80.2	1.5	4.9	7.7
2	2.0% LiF	85.8	61.3	61.5	88.7	2.0	4.4	7.0
2	2.0% CaF_2	-	78.5	51.8	74.4	1.6	5.6	8.8
2	5.0% CaF_2	93.0	93.7	65.6	84.1	1.4	4.5	8.0
2	10.0% P_2O_5	94.6[1]	100	61.1	94.8	1.2[2]	4.5[2]	6.7[2]
2	17.4% P_2O_5	97.6[1]	100	75.3	97.0	1.1[2]	3.9[2]	6.9[2]

[1]Overall (includes P_2O_5 in clay plus P_2O_5 added)

[2]Net (includes only P_2O_5 from clay)

SECTION VII

DISCUSSION OF RESULTS

The matrix samples used in this project were selected to reflect the major types of phosphate deposits found in the Florida Bone Valley formation. Variations in this deposit involve mainly the different types of clay, attapulgite, montmorillonite and kaolin, and weathering of the pebble fraction. All these requirements were met by the samples as evident from Table 6 (page 19).

Matrix Upgrading

From the beginning of the project it was apparent that the removal of nonphosphate components from the matrix prior to calcination was highly desirable for two reasons. First, to minimize fuel costs of the calcination and second, to eliminate some of the metal impurities such as iron, aluminum, and magnesium.

Essentially all methods - other than wet scrubbing - for separation of matrix components require a nearly dry matrix. Due to the high water table found in the Florida phosphate field, the matrix deposits contain from 30 to 60% by weight water. Drainage of the water from piled matrix is generally poor and depends mainly on the degree of clay contamination. Most matrix samples do not drain to less than 20% on piling above ground.

All matrix samples had to be dried to 3-5% moisture before separation tests could be performed. Mild attrition prior to or combined with air classification proved most effective in removing the major portion

of clay from the matrix. The problem was really not how much clay could be removed rather than to achieve the removal at a minimum phosphate loss. This correlation is evident from Table 8 (page 24) which lists the composition of material separated by air classification over a fluidized bed. The clay content can be judged from the aluminum concentration. Accordingly, only 4.9% of the matrix phosphate was lost when 20% of the original clay content was removed using unground matrix. When approximately 80% of the clay was removed by grinding the matrix prior to air classification, the phosphate loss increased to 27.7%.

Any successful method for the clay separation is highly dependent on finding selective grinding treatment which breaks up the clay particles and removes them from the phosphate pebble without disintegrating phosphate particles.

Of the series of grinding methods evaluated, namely, disk grinding, impact grinding, and tumbling in a ball mill, the latter provided the most selective disintegration. As evident from Table 12 (Appendix A), at approximately equal clay removal (80%), the phosphate loss upon air classification was 31.3% with impact crushing but only 18.3% with tumbling. A two-step treatment in which the matrix was slightly ground by tumbling, dedusted by air classification, and the whole process repeated once more, gave better results than a more intensive one-step process.

The clay removal for the purpose of reducing fuel cost in the calcination is readily accomplished. However, there are two other reasons for the clay separation which require a better than 90% clay removal to be effective. One is the objective of improving the P_2O_5/Al ratio of the matrix. Calculation of the P_2O_5/Al ratio as a function of clay removal indicates that a substantial improvement is realized only at a clay removal exceeding 80%, as shown in Figure 17. The other reason for attempting a clay removal of more than 90% is related to the separation of sand by electrostatic methods.

The sand separation by dry methods is limited to electrostatic separation techniques. However, work at USS Agri-Chemicals and at the Mineral Resources Research Center at the University of Minnesota established that the presence of small quantities of clay can be quite detrimental to the efficiency of the process. Residual clay coating of the phosphate particles interfered with the development of different electrostatic charges on the phosphate and sand particles.

When a vigorous wet scrubbing was applied to the test matrix prior to electrostatic treatment, the interference was completely eliminated, as evident from Tests A and C of Table 15 (Appendix A).

The problem of clay interference in the electrostatic sand separation can be mininized or completely eliminated by combining the drying and grinding steps. Such a process was described by Joe D. Clary et al. in U. S. patent 3,329,351. In this case, the wet matrix was introduced into a vertical attrition column positioned on top of a fluidized bed dryer.

FIGURE 17

CALCULATION OF P_2O_5/AL RATIO VERSUS CLAY REMOVAL

ATC 326-13

A high-velocity air stream was recirculated through the column which provided impact grinding by blowing the matrix against an impinger plate and carrying -1/4 in. material out through the top where it was separated into dust (clay) and matrix in cyclones. Sand contained in the phosphate fraction was successfully separated by electrostatic treatment.

Consultation with one of the engineers who operated this process at the pilot-plant level (800 pounds per hour) revealed that no problems with clay coating were observed. Consequently, no additional effort was made during the course of this project to overcome the clay interference encountered at USS Agri-Chemicals and at the Minnesota Mineral Resource Research Center. It is most likely the combined drying and grinding operation of the Clary process which prevents the formation of clay coating. Apparently, particle size reduction at the elevated temperature in the presence of a high-velocity air stream alleviates the problem.

Calcination and Digestion Performance

The major objective of this project was to achieve a digestion of matrix which would produce a filtrable gypsum slurry and to insolubilize the metals to yield a phosphoric acid of acceptable purity level. The present commercial phosphoric acid production was selected as a reference. Current processes recover about 65% of the total P_2O_5 value from the matrix and yield an acid quality corresponding to the following P_2O_5-to-metal weight ratios before concentration or clarification of the acid.

$P_2O_5/Fe = 40$

$P_2O_5/Al = 50$

$P_2O_5/Mg = 100$

Expressing the metal solubilization relative to that of P_2O_5 gives a more informative number than absolute solubility figures, since it is the ratio of P_2O_5 to metal which actually determines the quality of the acid. For this reason, most of the data in this report representing metals solubility are expressed as the P_2O_5-to-metal ratio as well as in concentration percent.

The process performance in calcination and digestion is subject to a large number of process variables. Major process parameters were established in a series of screening experiments, where a total of seven variables were evaluated for their dominance in the over-all process. As described in more detail in Section VI, the estimated variables were studied at two levels according to a fractional factorial design using a one-eighth replicate of the 2^7 factorial[3].

The results, as summarized in Table 18, revealed that the major variables were calcination temperature, particle size in calcination and digestion, and, to a lesser degree, acid strength in the digestion. To simplify and optimize the experimental work, all subsequent tests were carried out at only one particle size (-100 mesh), and at a fixed acid strength of 2.5% SO_4^{--}. The smaller particle size (-100 mesh) was selected because of the improved P_2O_5 extraction.

A comparison with Table 17 (page 31) shows that in the screening experiments the stipulated P_2O_5/Fe ratio (>40) was met in experiment Nos. 6, 9, and 12, and for P_2O_5/Mg (>100) in experiment No. 2. The best P_2O_5/Al ratio was 16.9 in experiment No. 2, which is far from the stipulated value of 50.

From the results of the screening experiments it became apparent that the greatest improvement in metals rejection would be necessary for aluminum. Consequently, subsequent work was aimed mainly at identifying the minerals containing aluminum and to characterize their behavior during calcination and digestion.

The objective of obtaining well-filtering digestion slurries was readily accomplished. All test slurries filtered equally well or better than commercial process gypsum slurries (350 GPH/ft^2). Thus, no detailed evaluation of the influence of calcination parameters on the filtration rate was made. The calcination treatment apparently completely destroyed the tendency of clays to swell and interfere in the filtration.

To identify the calcination response of different matrix components, the matrix was separated into a -150 mesh fraction, which consisted mainly of clay, and a +150 mesh fraction containing most of the phosphate. These two fractions are referred to as the "clay" and the "low-clay" fractions.

A full scan of the temperature response of these two fractions by differential thermal analysis[4] (DTA) indicated reactions or phase transformations as listed in Table 19 (Appendix A). As evident from the data, DTA does not produce a specific pattern according to the type of clay. Thermal changes up to 150°C are due to surface water. The endotherm at 235-240°C represents loss of water of hydration. Reactions or transformations affecting the acid solubility of iron, aluminum, and magnesium occur at temperatures from 800 to 1200°C. These do not follow a consistent pattern[5], although some trends can be recognized. Montmorillonite clay, for example, gives an endotherm-exotherm combination at 850°C. This so-called S curve is claimed in the literature to be associated with the formation of spinel ($MgAl_2O_4$). However, the curve for the total matrix from which the montmorillonite clay originated does not exhibit this pattern. No particular DTA peak is associated with apatite. Similarly, wavellite ($4\ AlPO_4 \cdot 2Al(OH)_3 \cdot 9H_2O$) in the matrix (IMC) does not show the same response as a sample of pure wavellite. For these reasons, differential thermal analysis was used in this work only to a limited degree.

Calcination tests with the USSAC matrix using the low-clay and the clay fractions showed that the practical temperature range can be limited to 800-1100°C. As evident from Figures 4 and 5 (pages 35, 36), no substantial decrease in acid solubility of iron, aluminum, and magnesium occurred below 800°C.

As a matter of fact, there was indication that the solubility actually increased up to about 800°C. Above 800°C a strong decrease was observed, reaching a minimum at 875°C for the low-clay fraction and at 900°C for the clay fraction. Calcination temperatures above 1100°C. caused sintering. Thus, calcination tests were limited to 1100°C since it was felt that a sintered charge posed unacceptable economic penalties.

The effect of calcination time on the acid solubility of iron, aluminum, and magnesium was evaluated in a more detailed study. The results are presented in Figure 16 (page 38). Accordingly, a calcination time of 30 minutes is sufficient to achieve minimum metals solubility. The curves for the 1000°C calcination show a distinct minimum at 1 hour, after which the solubility increases again. This response is probably less a function of time, rather, it seems to be the result of the temporary exposure of the samples to 800-900°C during warmup. Additional tests confirmed that the minimum acid solubility produced by calcination at 875°C is not permanent. Reheating to above 875°C leads to increased solubility, as apparent from data of Table 20 (Appendix A).

The phenomenon of reversible metals solubility discredits the commonly claimed spinel formation as the reason for a change of aluminum and magnesium solubility. If spinel were the acid-insoluble aluminum and magnesium compound formed during heating to 875°C, subsequent exposure to higher temperatures would not affect its acid solubility.

Based on the above observations, the series of matrix samples was calcined over a temperature range of 700-1100°C, using the total matrix as well as the separated low-clay and clay fractions. Calcination times were one hour. Most samples (Figures 6-10, Appendix B) followed the general pattern of a minimum solubility around 875-1000°C. This trend was particularly consistent in the clay fractions. All three types of clay, montmorillonite, attapulgite, and kaolin responded in the same manner. However, for unexplained reasons, the clay fraction of the USSAC matrix (montmorillonite) showed the minimum solubility 100°C lower than all others.

The low-clay fractions gave a minimum only in two cases (USSAC, IMC); the others exhibited a continuous decrease in solubility with increasing temperature up to 1100°C. It is possible that the minimum of the USSAC and IMC samples was caused by the presence of some residual clay.

The total matrix samples usually produced the additive result of the low-clay and clay fractions, as would be expected. One exception was the Borden matrix which did not reflect the strong reduction in solubility indicated by the separate clay and low-clay fractions.

Because of the difference in optimum temperatures for the low-clay and the clay fractions, the best over-all metal rejection was achieved when each fraction was calcined individually at the respective temperatures. Subsequent digestion could then be performed with the combined fractions. Another exception - this time in

a positive way - was the aluminum response of the IMC matrix. As evident from Figure 9 (Appendix B), the aluminum solubility of the total matrix was lower than the corresponding additive total of the low-clay and clay fractions.

In summary, all three metals responded to the calcination treatment. At optimum conditions, iron, aluminum, and magnesium solubilities were reduced to 30-60% of the total present. Depending on the type of mineral in which the metal was present, either of three metals could give the greatest reduction in solubility. Clay fractions showed usually a greater response than the low-clay fractions. Of the various types of clay, the response decreased in the order montmorillontie, attapulgite, kaolin. The poor response of allophane - an amorphous form of montmorillonite - as in the case of the American Cyanamid matrix (Figure 8, Appendix B) may be due to the presence of wavellite.

The better response of the clay fractions as compared to the low-clay fractions is most likely due to the fact that clays contain a mixture of metal ions in close proximity to silicate. And, the metal ions are relatively mobile. Whereas, metals in the phosphate form such a wavellite, geothite, etc., depend on particle-particle interaction to form the acid-insoluble compound. Consequently, higher temperatures are necessary to provide the required mobility. This is in agreement with the results showing that the low-clay fractions give the better insolubilization the higher the temperature.

No positive identification of species representing the acid-insoluble metal derivatives was made. Only mullite ($3Al_2O_3 \cdot 2SiO_2$) appeared as an X-ray active form[6]. Most other acid-insoluble species formed at 875°C were X-ray inactive. Crystalline phases appeared at 1000-1100°C, but these were associated with an increase in solubility and therefore could not represent the sought-after compounds.

The calcination treatment caused volatilization and/or decomposition of several matrix components. A typical weight loss of the dry matrix ranged from 7 to 9%. The volatilized compounds consisted of silicon tetrafluoride, formed by the interaction of fluoroapatite with silicates or quartz, and carbon dioxide resulting from the decomposition of carbonates and from oxidation of organic matter. Fluoride volatilization during calcination amounted to 25% of the matrix fluoride at 980°C and 32% at 1100°C. The evolution of fluoride occurred very rapidly. It was usually completed within 10 minutes.

Attempts to improve the metals insolublization by additives were essentially futile. So-called mineralizers[7] and fluxes which promote solid-state reactions or lower the temperature at which these reactions proceed gave only marginal or no improvements at all. As listed in Table 22 (page 40), magnesium oxide, lithium fluoride, fluorspar (CaF_2), and phosphoric oxide were tested. There are indications that reducing agents might be effective to decrease the solubility of iron.

All preceding experimental results were obtained by the use of a hydrochloric acid digestion, aided by the addition of an oxidizer such as nitric acid or hydrogen peroxide. This method was selected for the initial scanning of the bulk of calcination samples in place of the time-consuming phosphoric-sulfuric digestion which gives a more representative indication of plant-scale performance. A comparison of both methods established the suitability of the hydrochloric acid digestion as demonstrated in Figure 3 (page 34). Both methods reflected the response to calcination relative to the temperature dependence and therefore were useful to interpret data. The only difference was in the absolute level of solubility. Predictions relative to yield have to be based on the phosphoric-sulfuric acid digestion data presented in Figures 11-15 (Appendix B). As a rule, the phosphoric-sulfuric acid digestion gives a slightly better metals rejection than the hydrochloric acid method. In particular, the solubility of iron is often greatly reduced as in the case of the American Cyanamid (Figure 13, Appendix B) and the IMC (Figure 14, Appendix B) matrices.

Chemically pure phosphoric acid was used in these digestions. Since the plant-scale process employs wet-process acid, that is, acid containing iron, aluminum, and magnesium, one might expect a better metals rejection than with chemically pure acid. A brief test indicated a marginal difference between the two acids, if any.

Data of the preceding studies were expressed as percent solubilization of the total metals of the matrix or its fraction. This unit is best suited to discuss the calcination performance and follow the effect of process parameters. The process performance with respect to acid quality is better recognized in terms of P_2O_5-to-metals ratio. Therefore, results of the calcination-digestion experiments were also expressed in relation to the phosphate solubilization which is actually the true measure of acid quality. Figures 18-22 (Appendix B) summarize the finding for the hydrochloric acid digestion and Figures 23-27 (Appendix B) for the phosphoric-sulfuric acid digestion. It becomes immediately apparent that despite the relatively good metals insolubilization, the quality of the produced phosphoric acid is in most cases short of the stipulated specifications. Although aluminum gave, on a percentage basis, reduction in solubility similar to that of iron and magnesium, on a P_2O_5/metal basis it is mainly aluminum which failed to reach the goal. The reason for this is the relatively high aluminum level of most matrix samples.

For example, in the case of the USSAC matrix, which contained P_2O_5-to-metal ratios of 8.2, 4.3, and 24.2, respectively, for iron, aluminum, and magnesium, the necessary improvement factors to reach the stipulated quality were 4.8 for iron, 11.6 for aluminum, and 4.2 for magnesium. A similar situation existed for the other matrix samples.

A comparison of the total matrix versus low-clay fractions revealed that the clay removal sometimes improved the P_2O_5-to-metal ratios (USSAC, Borden, Mobil) and sometimes worsened them (P_2O_5/Fe in American Cyanamid, IMC matrix). This is due to the different behavior of metal-containing minerals on air classification. If the clay separation removed a substantial portion of those minerals which did not respond to calcination, the P_2O_5-to-metal ratio of the remaining low-clay fraction improved, and vice versa. The following summary (Table 23) shows which fraction - low-clay or total matrix - gave the best P_2O_5-to-metal ratios, and at what calcination temperature.

TABLE 23

OPTIMUM PERFORMANCE SUMMARY

Source	Fraction	P_2O_5-to-Metal Ratio			Calcination
		Fe	Al	Mg	Temp. °C
USSAC	Low-Clay	18	18	68	900
BORDEN	Total Matrix	143	41	280	900
AM. CYANAMID	Low-Clay	51	15	108	1000
IMC	Total Matrix	79	8	97	1000
MOBIL	Low-Clay	24	14	9	1000

As evident from the data, the stipulated specifications were met in three out of five cases for iron and magnesium, and was approached in one case for aluminum.

The matrix from the Mobil mine can not be considered a typical phosphate matrix. As described in more detail in SECTION IV, this sample was evaluated only because it contained attapulgite clay. It is doubtful that this matrix could be upgraded by any method, including wet processing.

SECTION VIII

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   A 2^7 factorial design consists of a series of experiments which contains all the combinations of the seven variables at the high and the low level.

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SECTION IX

GLOSSARY

Beneficiation - Upgrading of ore by removal of inert material.

Flotation - Separation of ore and inert material in an aqueous slurry.

Lateritic Weathering - Transformation of ore particles on the surface only.

Matrix - Total ore body as mined from the deposit.

Middling - Middle fraction of a sample series.

Mineralizer - Additive which facilitates a solid-solid reaction or lowers the minimum temperature at which the reaction takes place.

Phosphate Concentrate - Phosphate ore enriched by separation of inerts.

Riffling - Method of splitting a sample into two or more portions of equal composition by use of a mechanical device.

Slimes - Fine fraction (-150 mesh) from phosphate matrix suspended in water.

Tailing - End fraction of beneficiation process. In the case of phosphate ore, the tailing is mainly sand.

SECTION X

APPENDICES

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APPENDIX A

SUPPLEMENTARY TABLES

TABLE 9

EFFECT OF IMPACTOR RPM

ON MATRIX DISINTEGRATION

(ATC 322-39)

Treatment Mode	Tyler Mesh	% P_2O_5	% Weight	% P_2O_5 Distn.	% Dedusting Efficiency
Sample	+48	8.90	40.05	37.47	
" As Is"	-48+100	10.59	40.59	44.85	
	-100+200	9.04	13.25	12.63	
	-200	7.87	6.11	5.05	
Disintegrated	+48	8.82	38.09	35.20	
at 2000	-48+100	10.54	40.96	45.25	
RPM &	-100+200	9.58	13.53	13.60	
dedusted	-200	7.85	0.70	0.52	
	Clay	7.68	6.72	5.43	89.54
Disintegrated	+48	8.65	20.46	18.34	
at 4000	-48+100	10.31	47.84	51.09	
RPM &	-100+200	10.08	11.00	11.50	
dedusted	-200	8.95	0.32	0.31	
	Clay	8.90	20.38	18.76	82.48

TABLE 10

TIME EFFECT OF CERAMIC TUMBLING

(ATC 322-39)

Time, min	Tyler Mesh	% P_2O_5	% Weight	% P_2O_5 Distn.
15	+48	9.33	24.98	24.07
	-48+100	10.48	49.63	53.72
	-100+200	8.42	17.11	14.88
	-200	8.58	8.28	7.33
30	+48	9.85	16.78	16.89
	-48+100	10.51	48.23	51.89
	-100+200	8.87	22.08	20.06
	-200	8.42	12.91	11.16
45	+48	9.90	14.58	14.30
	-48+100	10.19	51.54	52.14
	-100+200	10.56	22.73	23.83
	-200	8.82	11.15	9.73

TABLE 11

LOADING EFFECT OF CERAMIC TUMBLING

(ATC 322-39)

Charge, g	Tyler Mesh	% P_2O_5	Weight	P_2O_5 Distn.
650	+48	10.08	16.17	16.63
	-48+100	10.47	51.08	54.60
	-100+200	8.54	21.27	18.57
	-200	8.73	11.48	10.20
1500	+48	9.90	14.58	14.10
	-48+100	10.19	51.54	52.14
	-100+200	10.56	22.73	23.83
	-200	8.82	11.15	9.77
2000	+48	10.03	21.81	21.90
	-48+100	10.63	52.41	55.70
	-100+200	8.70	17.61	15.30
	-200	8.69	8.17	7.10

TABLE 12

COMPARISON OF IMPACTOR GRINDING VERSUS CERAMIC TUMBLING

(ATC 322-39)

Method	Tyler Mesh	% P_2O_5	% Weight	% P_2O_5 Distn.	% Clay Removal
4000 RPM Impactor	+48	7.57	12.36	9.74	
	-48+100	9.65	45.16	45.13	
	-100+200	10.76	12.47	13.87	
	-200	10.08	29.92	31.26	~80
Ceramic Tumbling, 2000 g 45 min	+48	9.48	24.75	24.15	
	-48+100	11.04	44.53	50.57	
	-100+200	8.85	7.64	6.99	
	-200	7.73	23.03	18.29	~80

TABLE 13

EXPERIMENTAL CONDITIONS OF ELECTROSTATIC SAND SEPARATION

Experiment No.	Electrode	Electrode Position[1]		Voltage	Feed Roller
320-47-4	Dielectric Rotary	4:00	3.5	-	Dielectric
-7	Huff Rotary	3:00	2.0	20,000	Dielectric
-13	Huff Rotary	4:00	2.0	20,000	Brass
-15	Huff Rotary	1:30	2.0	22,000	Brass
-16	Huff Rotary	1:30	2.0	22,000	Brass
-18	Huff Rotary	1:30	2.0	22,000	Brass
-19	Huff Rotary	3:00	2.0	22,000	Brass
-20	Huff Rotary	1:30	2.0	24,000	Brass
-23	Huff Rotary	1:30	1.2	16,000	Brass

[1] Listed as clock position and distance between electrodes in inches.

TABLE 14

SAND SEPARATION TESTS AT USS AGRI-CHEMICALS

Experiment No.	Matrix[1]	Pretreatment	Cut	% Weight	% P_2O_5	% P_2O_5 Distn.
320-47-4	Am. Cyanamid	Washed	Tailings	22.0	5.02	12.4
			Middling	72.0	9.55	77.7
			Concentrate	6.0	14.70	9.9
-7	Am. Cyanamid	Washed	T	23.8	8.25	24.0
			M	61.2	7.91	59.2
			C	15.0	9.20	16.8
-13	Am. Cyanamid	Washed	T	27.2	7.65	20.7
			M	45.4	10.43	47.3
			C	27.4	11.72	32.0
-15	Am. Cyanamid	Dedusted	T	57.6	10.25	57.1
			C	42.4	10.47	42.9
-16	Am. Cyanamid	Dedusted	T	47.7	10.65	49.5
			C	52.3	9.91	50.5
-18	IMC	Washed	T	40.0	5.66	26.7
			C	60.0	10.32	73.3
-19	IMC	Washed	T	9.4	6.00	6.6
			M	40.9	5.29	25.3
			C	49.7	11.72	68.1
-20	IMC	Dedusted	T	46.9	7.63	37.8
			C	53.1	11.12	62.2
-23	IMC	Dedusted	T	56.2	9.14	50.7
			C	43.8	11.41	49.3

TABLE 15

SAND SEPARATION TESTS AT MINNESOTA RESOURCES RESEARCH CENTER

(ATC 320-40)

			%						
Fraction[1]	Weight	P_2O_5	P_2O_5 Distn.	Al	Al Distn.	Fe	Fe Distn.	Mg	Mg Distn.
Ac	6.3	10.8	6.80	1.92	9.60	1.13	9.10	0.429	9.51
AM_1	48.7	10.06	49.00	1.42	54.92	0.854	53.33	0.323	55.28
AM_2	33.8	9.74	32.90	1.02	27.38	0.672	29.10	0.232	27.46
AT	11.2	10.09	11.30	0.917	8.17	0.592	8.46	0.200	7.75
Bc	11.5	15.51	17.23	0.977	14.18	0.638	12.33	0.224	13.07
BM_1	30.1	12.15	35.33	0.913	34.81	0.644	32.77	0.221	33.67
BM_2	35.3	8.63	29.53	0.652	29.11	0.552	32.94	0.166	29.65
BT	23.1	8.01	17.91	0.747	21.90	0.564	21.96	0.204	23.62
Cc	30.9	22.75	75.43	0.345	70.86	0.570	53.17	0.159	71.01
CM_1	9.1	17.03	16.63	0.293	17.88	0.473	12.99	0.120	15.94
CM_2	7.2	3.14	2.42	0.088	3.97	0.237	5.14	0.028	2.90
CT	52.8	0.98	5.55	0.020	7.28	0.179	28.70	0.013	10.14
Ec	20.1	19.87	37.36	0.795	24.28	0.662	23.05	0.179	22.64
EM_1	9.5	16.11	14.33	0.852	12.90	0.704	11.61	0.217	13.21
EM_2	11.7	10.31	11.33	0.686	12.14	0.633	12.82	0.172	12.58
ET	58.7	6.73	36.99	0.569	50.68	0.516	52.51	0.139	51.57

A = Sample tested as received
B = Sample was wet washed by jigging over a screen
C = Sample was subjected to shear scrubbing
E = Sample was attrition scrubbed

c = Concentrate
M_1 = Middlings
M_2 = Middlings
T = Tailings

TABLE 19

DIFFERENTIAL THERMAL ANALYSIS OF MATRIX SAMPLES[1]

(ATC 328-21)

	°C															
	115-120	135-140	150-155	170-180	235-240	330-340	500	535-540	575	780	810	850-860	870-880	930	960	1100
USSAC Clay (montmorillonite)		-			-				-			- (S-curve)	+			
USSAC Matrix		-			-				-							
IMC Clay (montmorillonite, kaolin)	-			-	-				-		+	- (S-curve)	+			-
IMC Matrix		-	-		-				-							
Borden Clay (kaolin)	-				-				-				+			
Mobil Clay (attapulgite)	-		-				-		-			+				
Mobil Clay + Apatite, ~50:50	-		-	-	-			-	-	-		+				
American Cyanamid Clay (allophane, wavellite)		-	-		-				-					+		
Wavellite, from Montgomery Co., Ark.					-	-			-						+	

[1] - = Endothermic
+ = Exothermic

TABLE 20

CALCINATION OF CLAY FRACTION AT TWO CONSECUTIVE TEMPERATURES

(ATC 321, p. 23)

Calcination Time, hr	Temp., °C	% Extraction(HCL-HNO_3 Digest.)				P_2O_5/Metal Weight Ratio		
		P_2O_5	Al	Fe	Mg	Al	Fe	Mg
1	875	-	30.4	11.9	14.6	3.8	22.0	41.0
1 1	715 875	83.0	30.3	11.1	14.6	3.8	24.0	41.0
1 1	715 1000	90.8	66.0	32.0	54.6	1.9	9.0	12.0
1 1	875 1000	91.1	65.2	31.9	52.4	2.0	9.1	13.0
1	1000	93.0	70.3	35.9	57.3	1.9	8.2	12.0

TABLE 21

CALCINATION OF MATRIX AT TWO CONSECUTIVE TEMPERATURES

(ATC 328-17, 18)

Calcination Time, hr.	Temp., °C	% Extraction (HCl Digestion)			P_2O_5/Metal Weight Ratio[1]		
		Al	Fe	Mg	Al	Fe	Mg
Uncalcined Matrix		93.7	103.0	97.5	4.6	8.0	24.7
1/2	875	42.0	59.3	40.0	11.7	14.4	66.0
1	875	40.9	55.8	39.0	12.1	15.3	67.8
2	875	40.2	56.2	37.7	12.3	15.2	70.1
1/2	1000	60.8	71.1	51.0	8.1	12.0	51.8
1	1000	77.0	80.9	70.2	6.4	10.5	37.6
2	1000	89.9	90.0	84.9	5.5	9.5	31.1
4	1000	91.4	87.6	87.2	5.4	9.7	30.3
1 1	715 875	38.8	56.0	39.2	12.7	15.2	67.3
1 1	715 1000	77.0	82.2	72.8	6.4	10.4	36.3
1 1	875 1000	64.1	76.0	55.9	7.7	11.2	47.3

[1]95% P_2O_5 extraction assumed in all cases.

APPENDIX B

SUPPLEMENTARY FIGURES

FIGURE 6

HYDROCHLORIC ACID DIGESTION
OF USSAC MATRIX

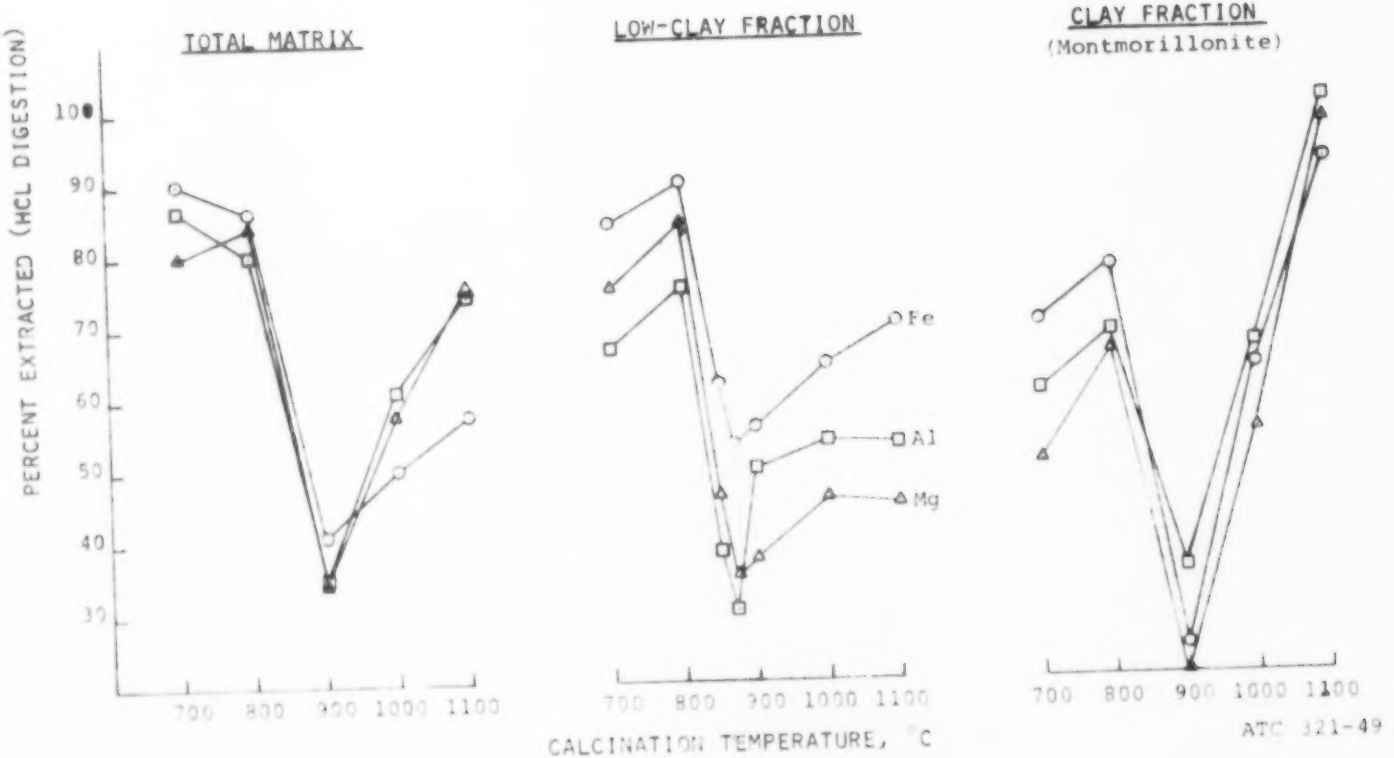

FIGURE 7

HYDROCHLORIC ACID DIGESTION
OF BORDEN MATRIX

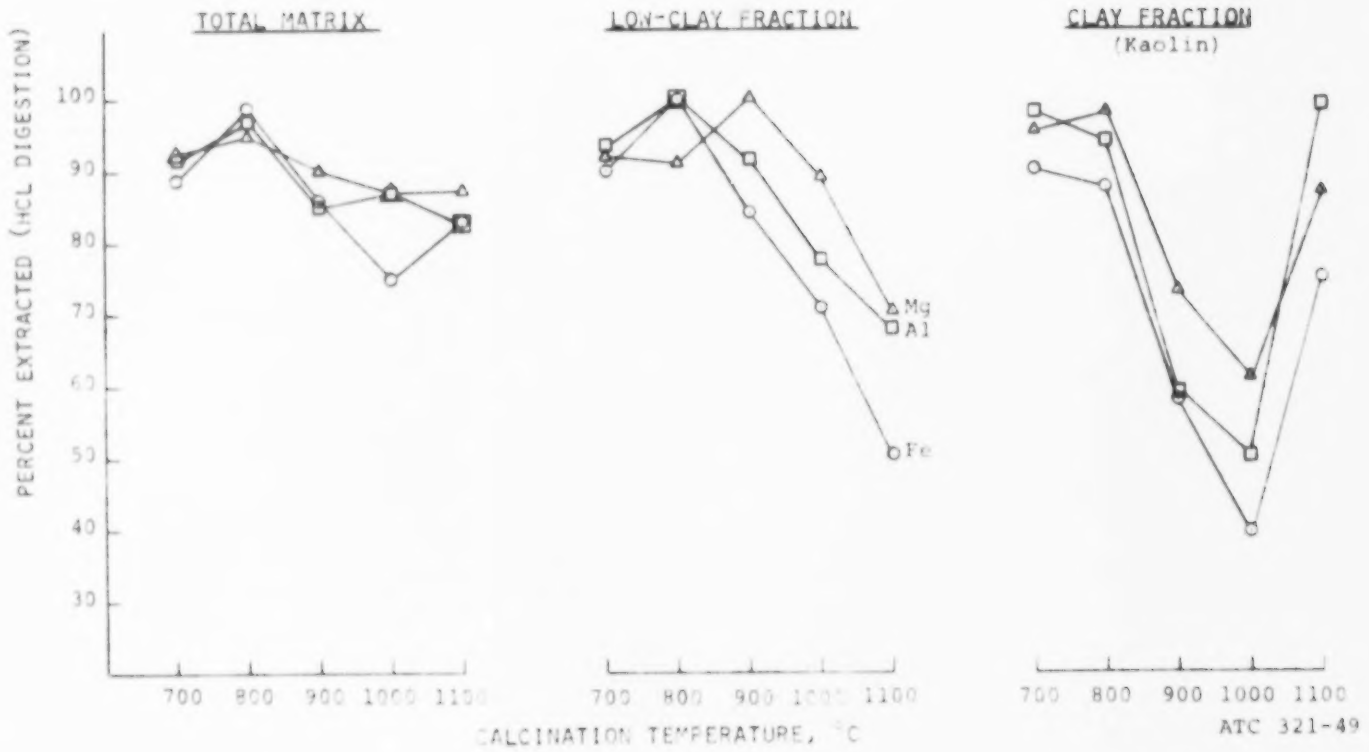

FIGURE 8

HYDROCHLORIC ACID DIGESTION
OF AMERICAN CYANAMID MATRIX

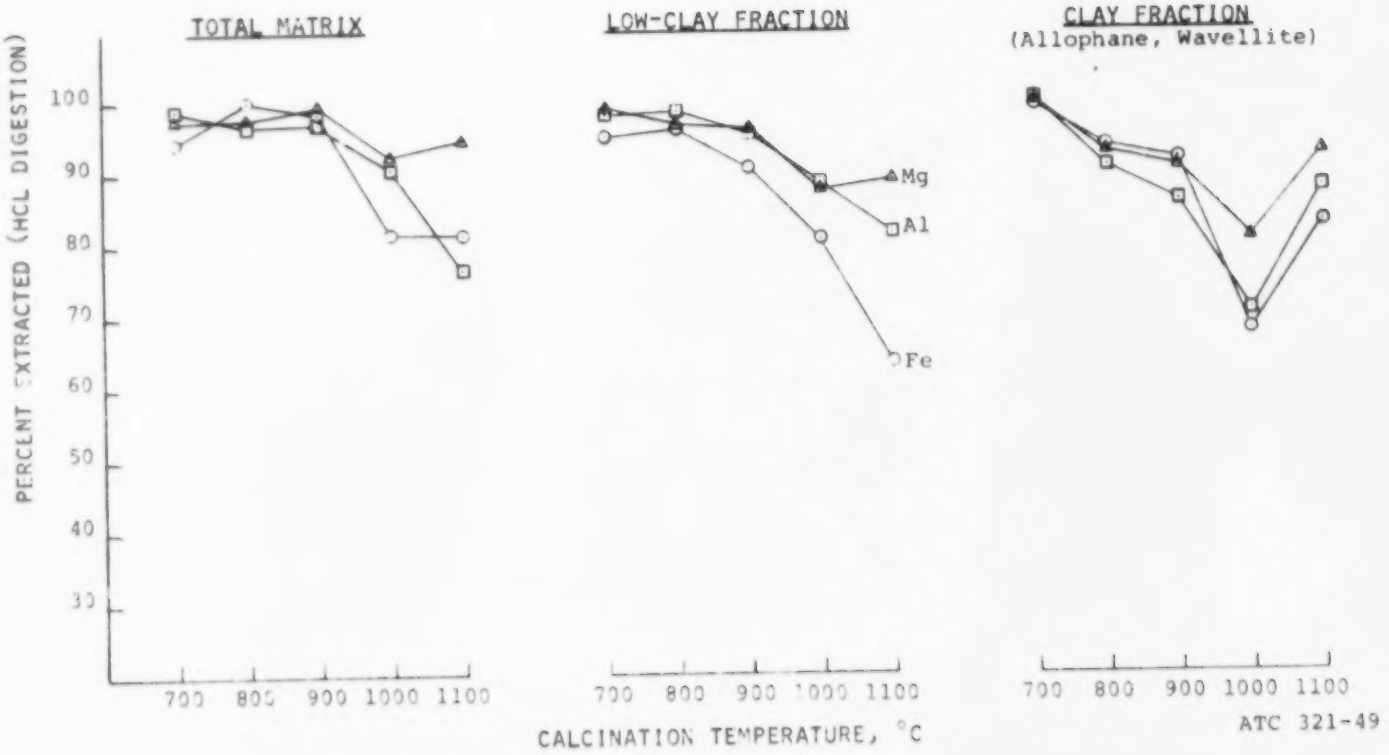

FIGURE 9

HYDROCHLORIC ACID DIGESTION
OF IMC MATRIX

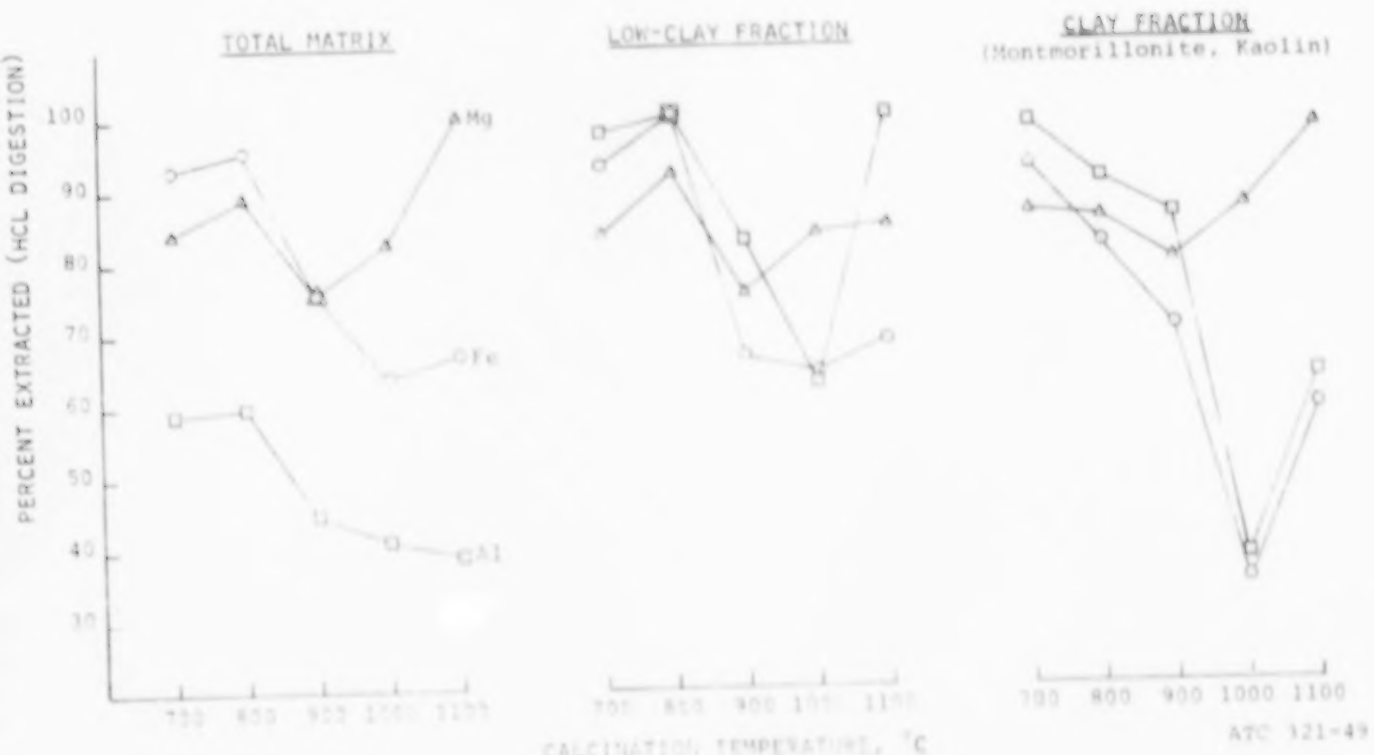

FIGURE 10

HYDROCHLORIC ACID DIGESTION
OF MOBIL MATRIX

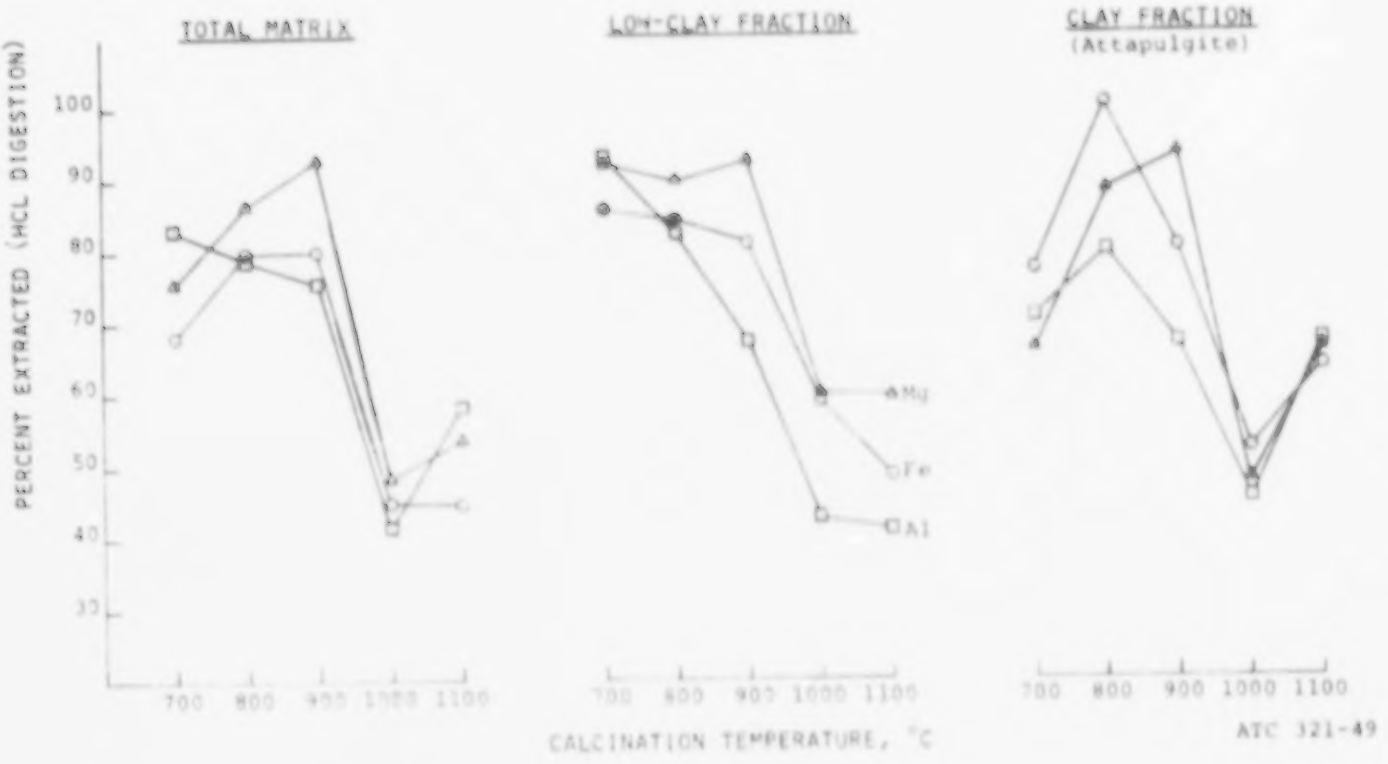

FIGURE 11

PHOSPHORIC-SULFURIC ACID
DIGESTION OF USSAC MATRIX

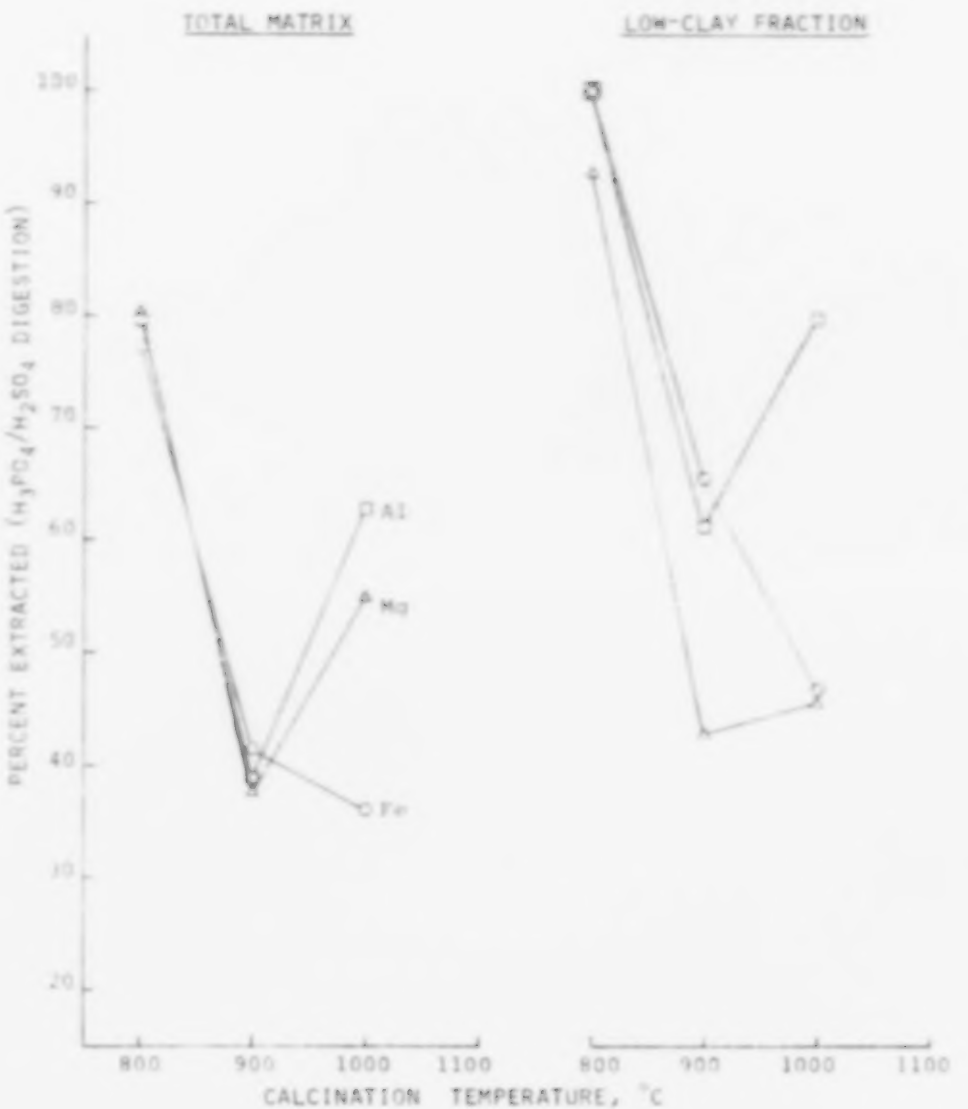

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FIGURE 12

PHOSPHORIC-SULFURIC ACID
DIGESTION OF BORDEN MATRIX

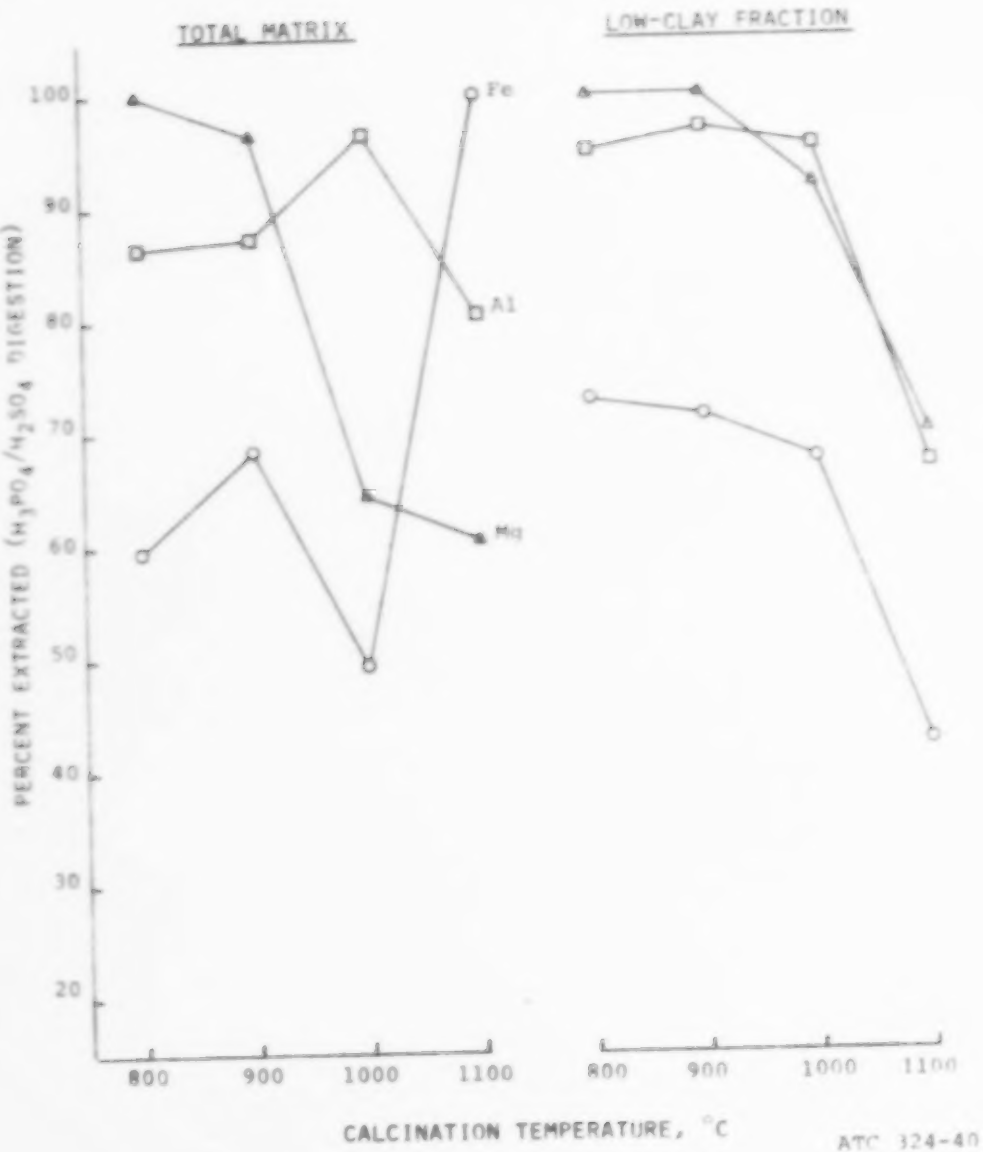


FIGURE 13

PHOSPHORIC-SULFURIC ACID DIGESTION
OF AMERICAN CYANAMID MATRIX

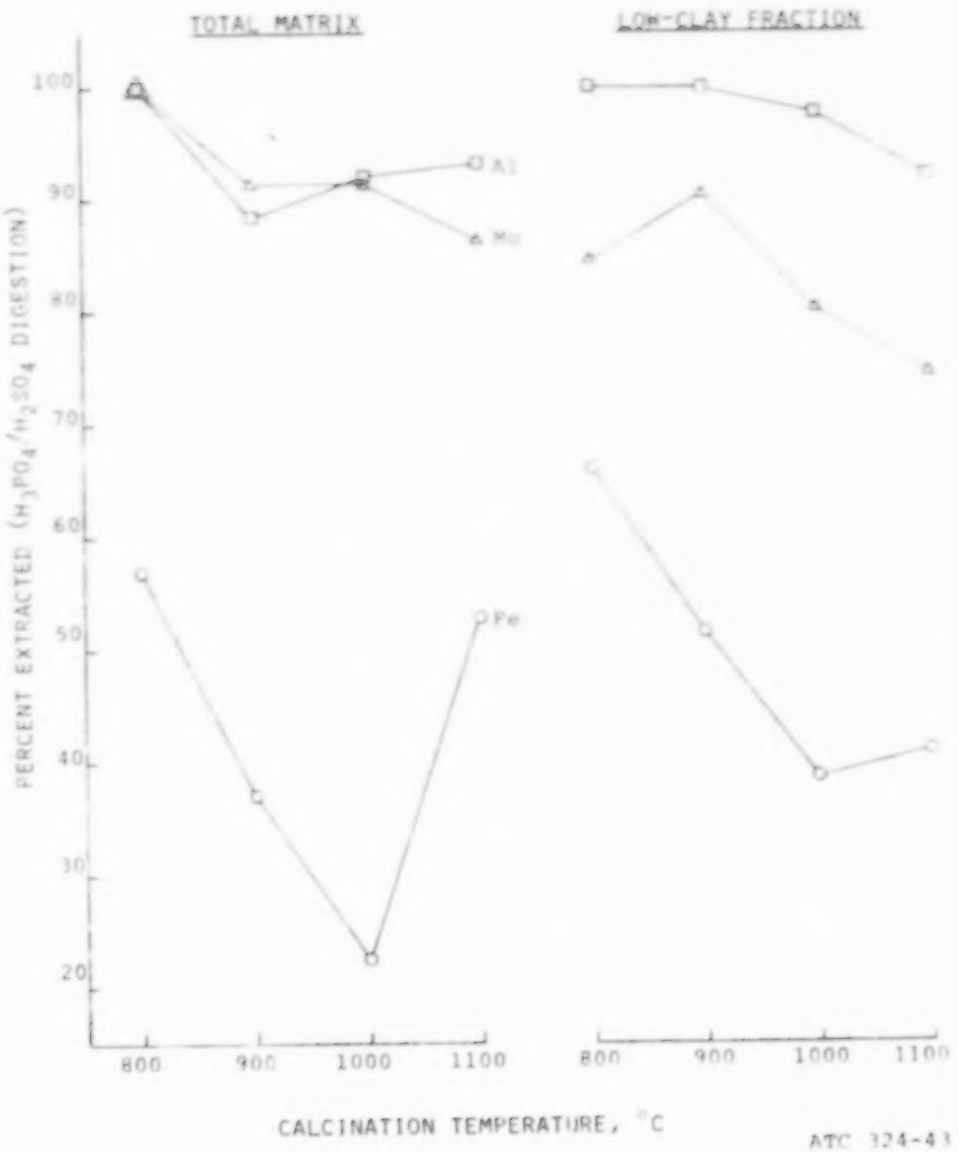


FIGURE 14

PHOSPHORIC-SULFURIC ACID
DIGESTION OF IMC MATRIX

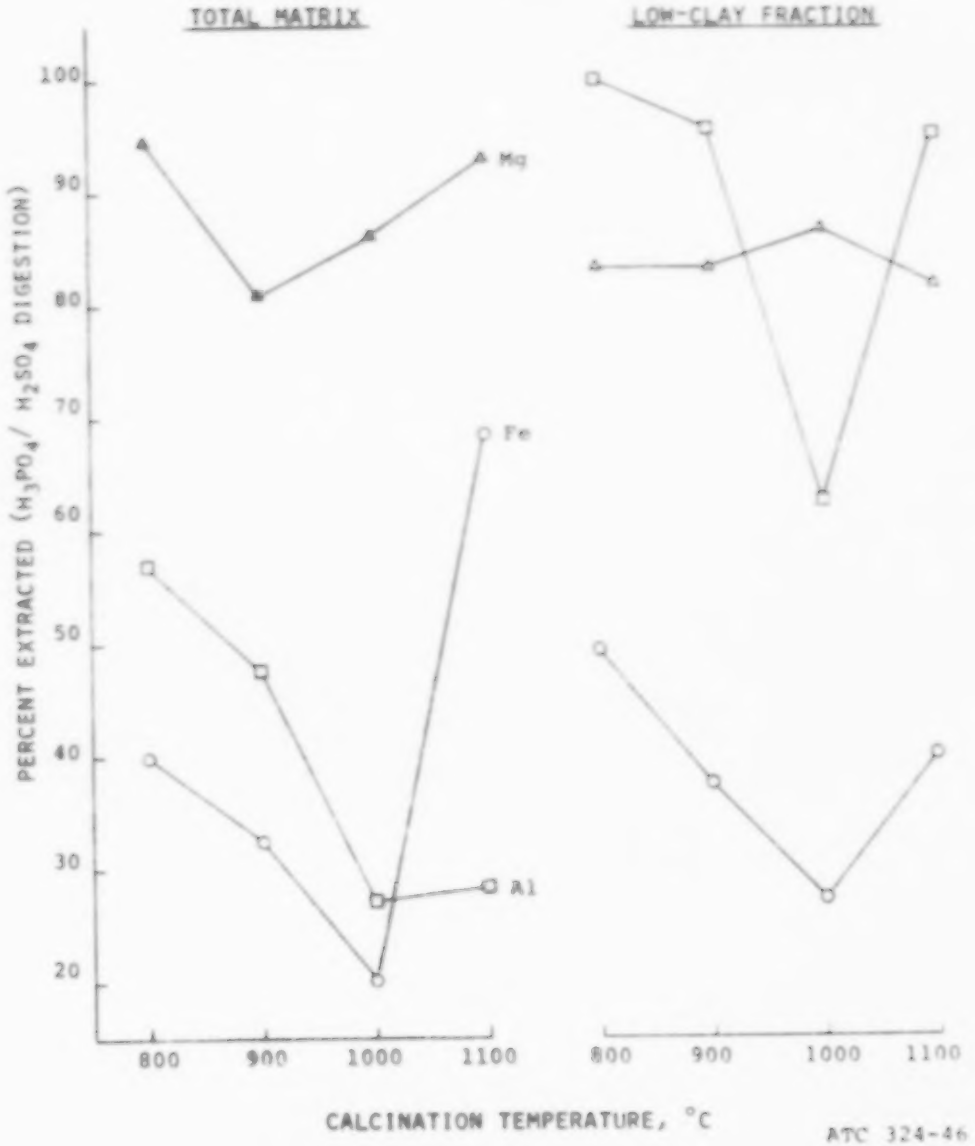
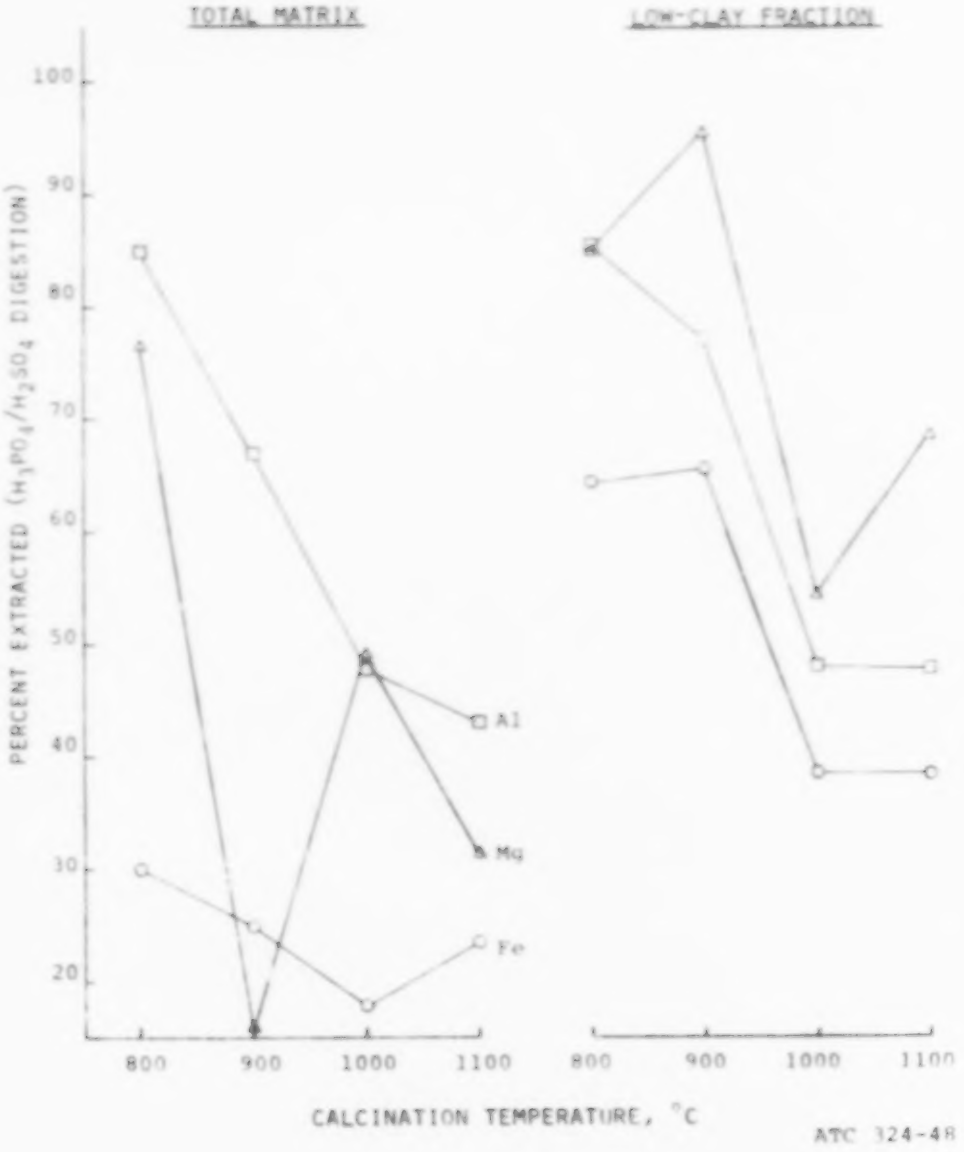


FIGURE 15

PHOSPHORIC-SULFURIC ACID
DIGESTION OF MOBIL MATRIX



ATC 324-48

FIGURE 18

P_2O_5/METAL RATIOS OF USSAC MATRIX

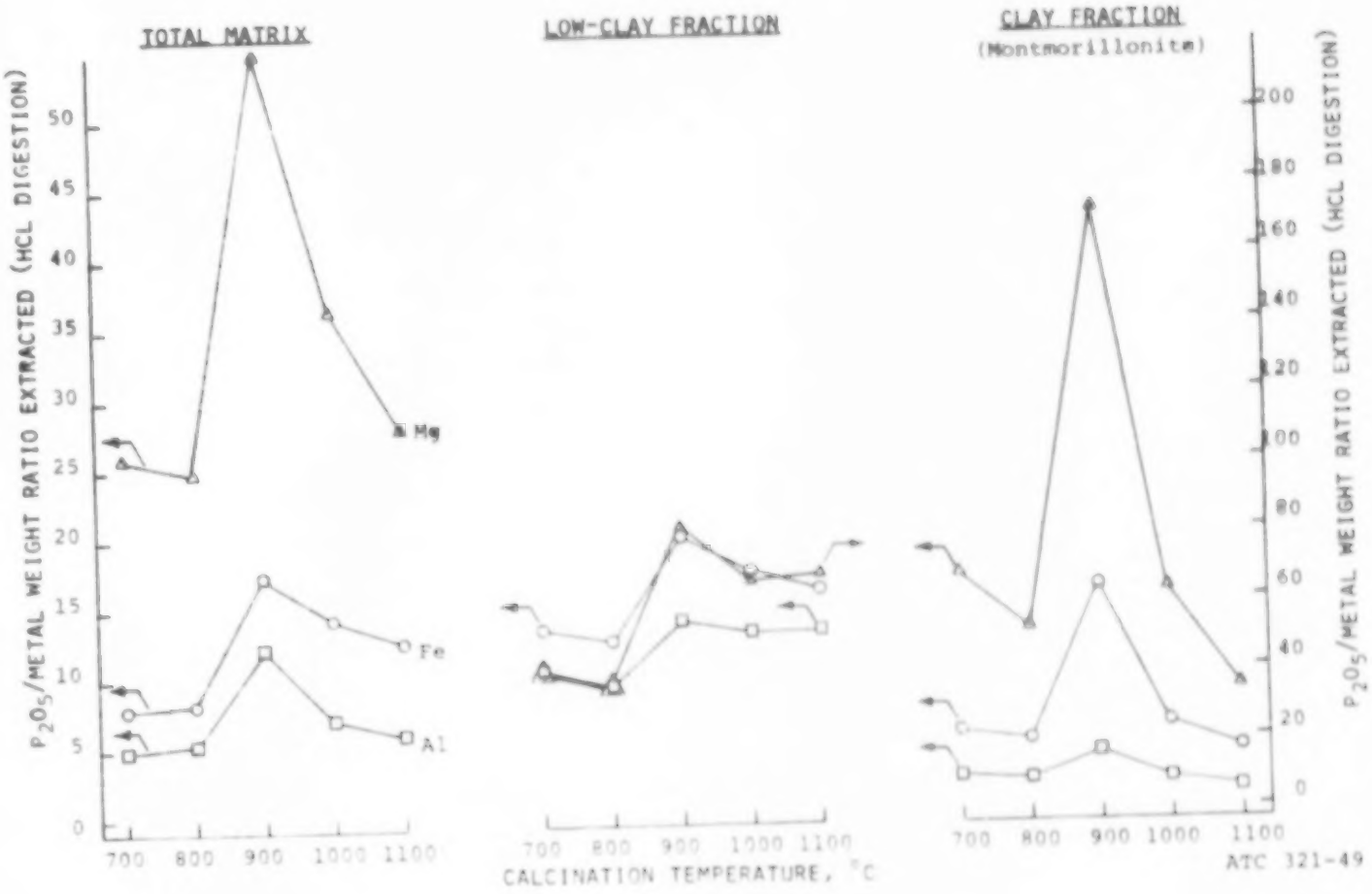
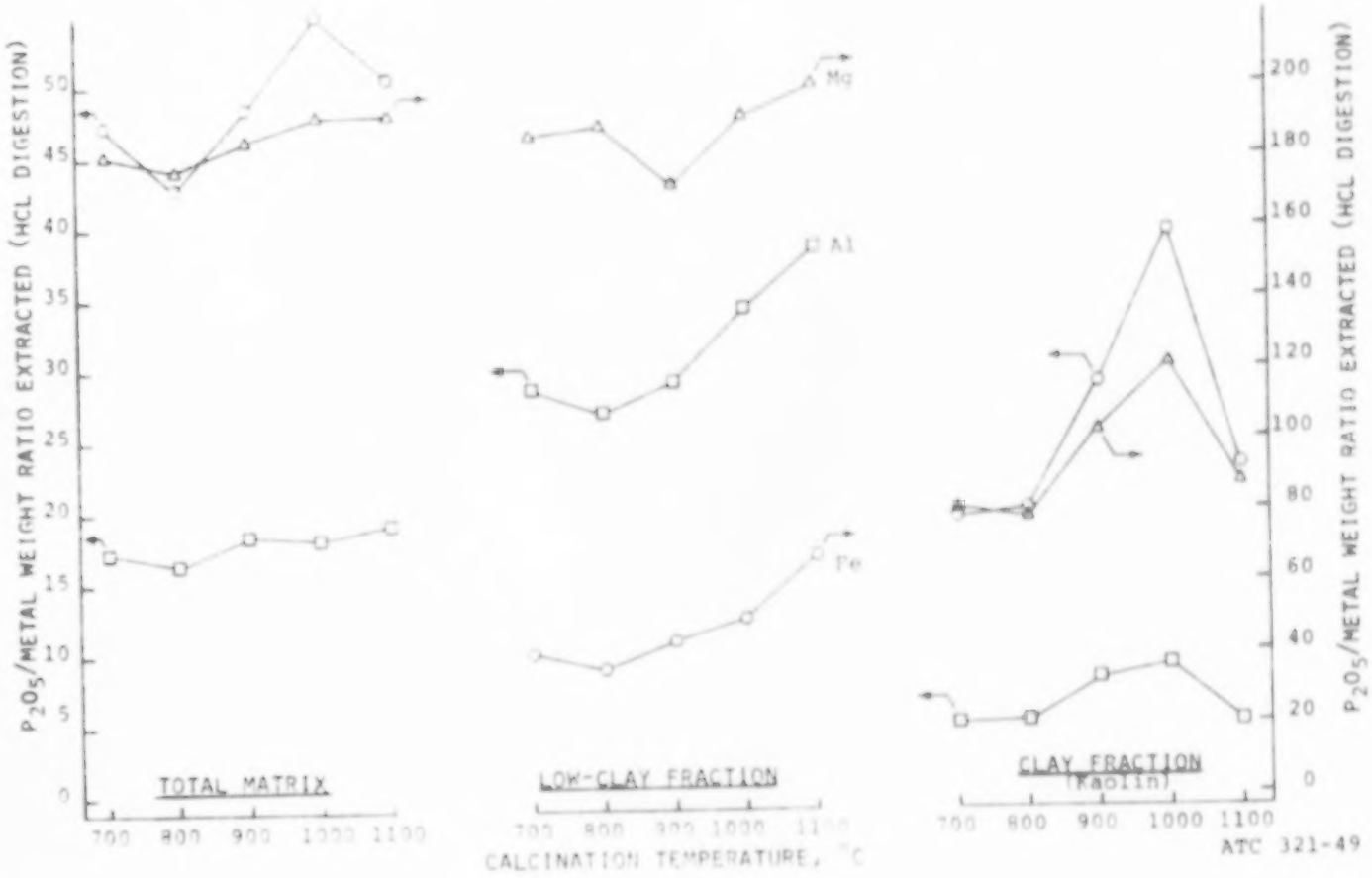


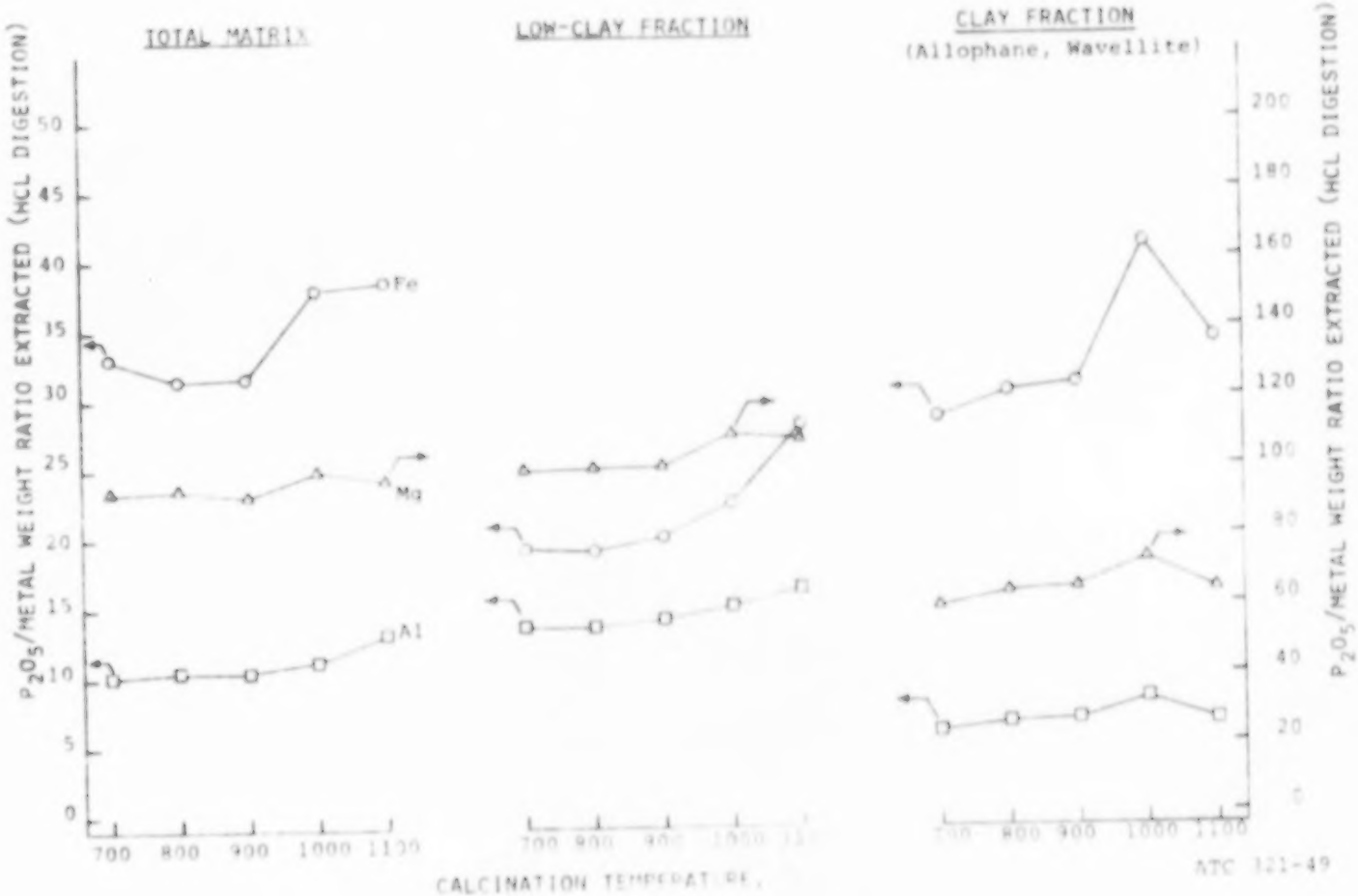
FIGURE 19

P_2O_5/METAL RATIOS OF
BORDEN MATRIX



FIGURE

P_2O_5/METAL RATIOS OF
AMERICAN CYANAMID MATRIX



ATC 121-49

FIGURE 21

P_2O_5/METAL RATIOS OF
IMC MATRIX

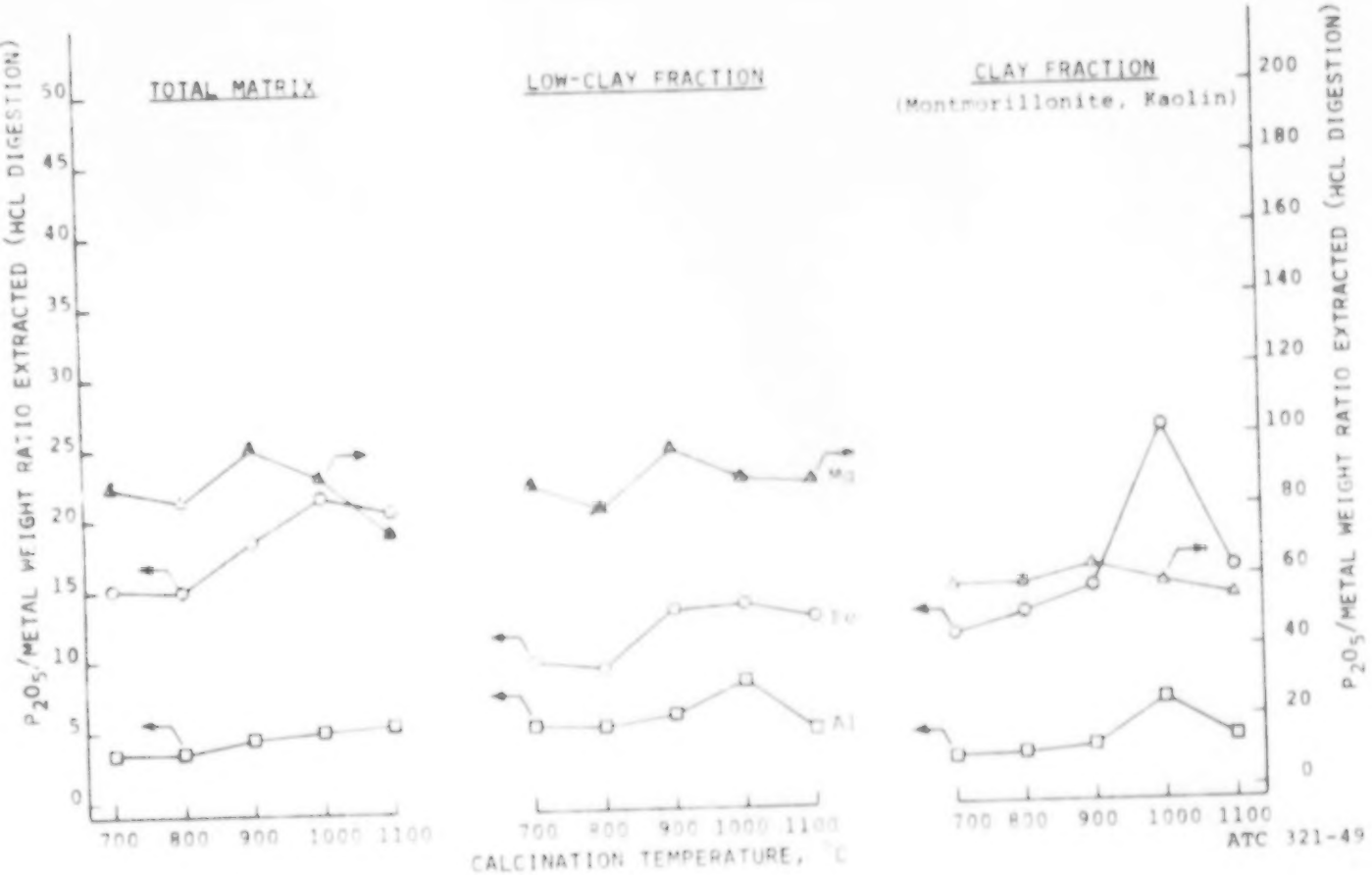


FIGURE 27

P_2O_5/METAL RATIOS OF
MOBIL MATRIX

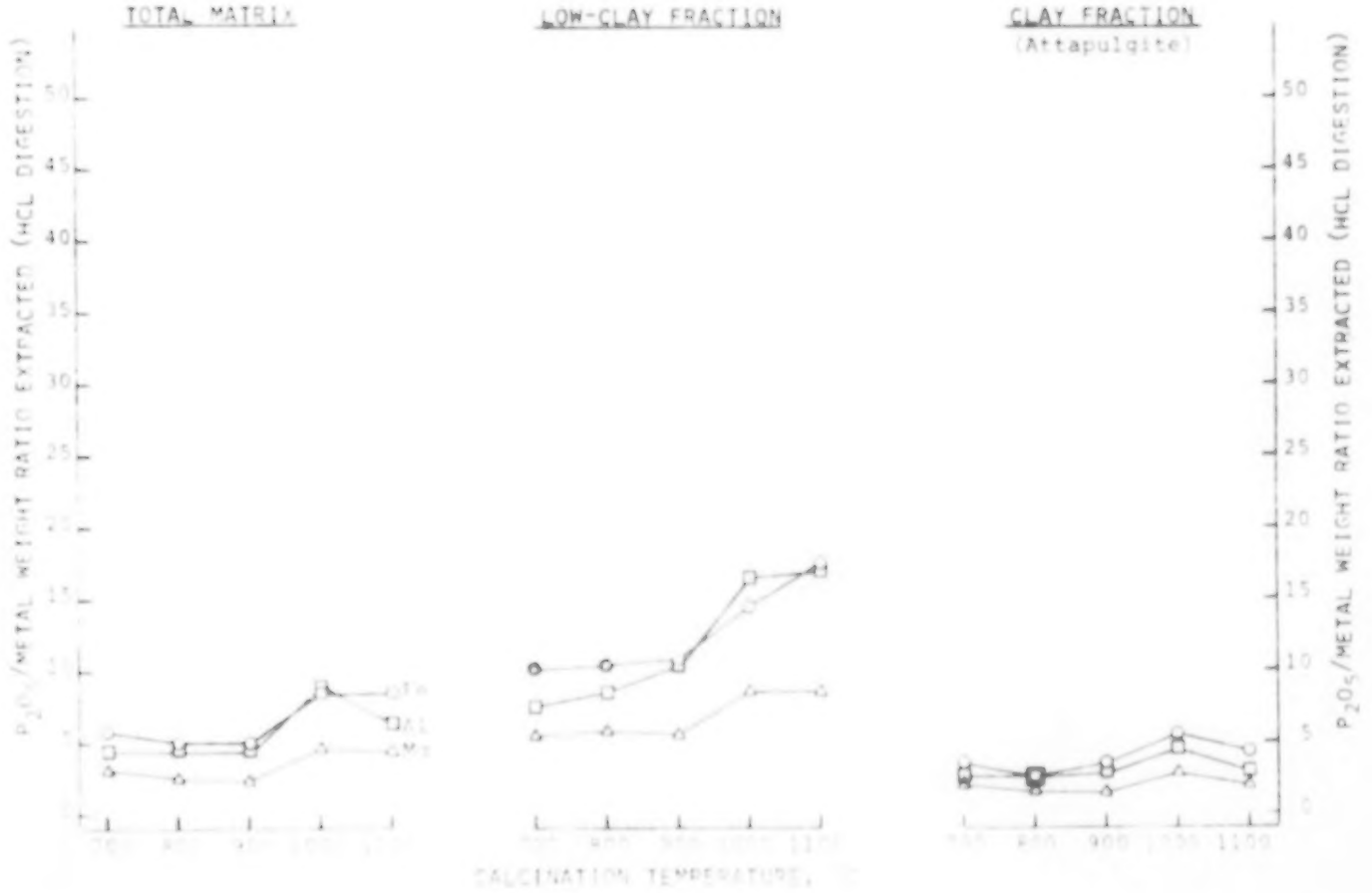
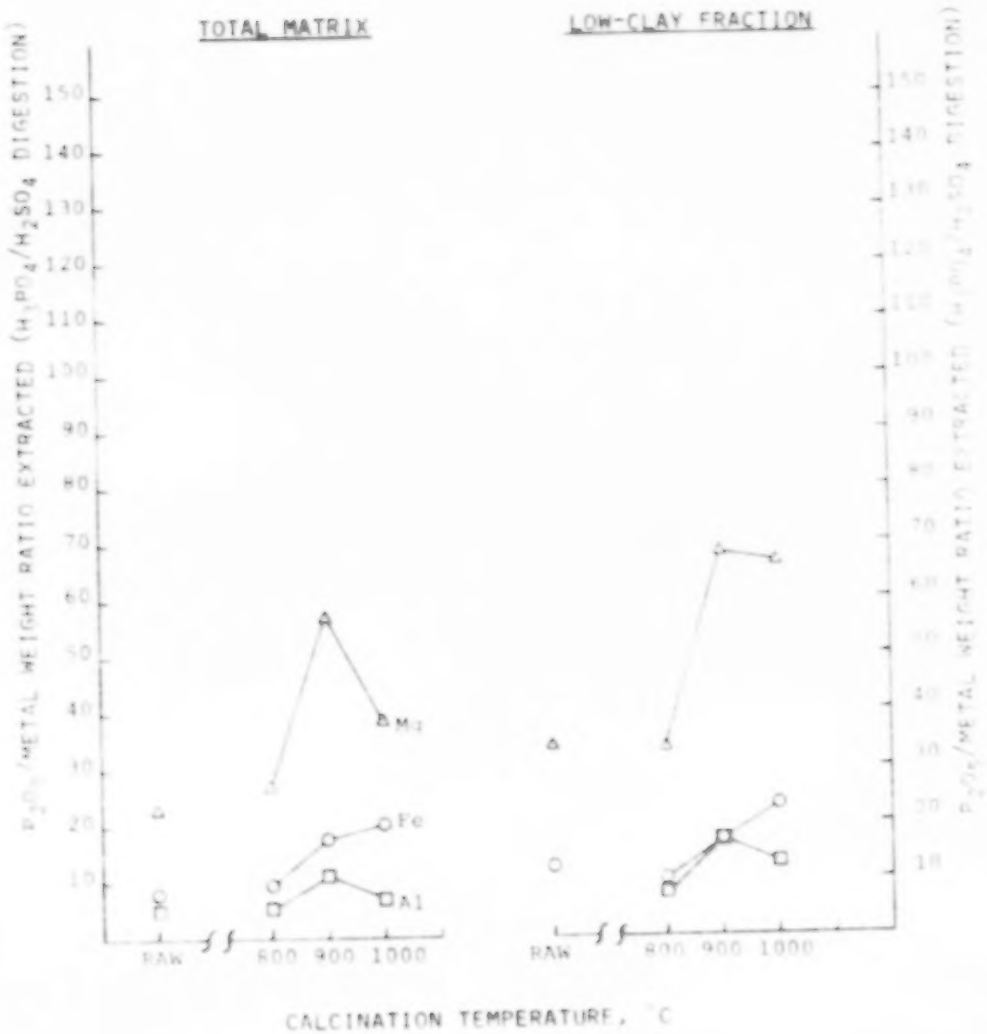


FIGURE 23

P_2O_5/METAL RATIOS OF
USSAC MATRIX



ATC 124-40

FIGURE 24

P_2O_5/METAL RATIOS OF
BORDEN MATRIX

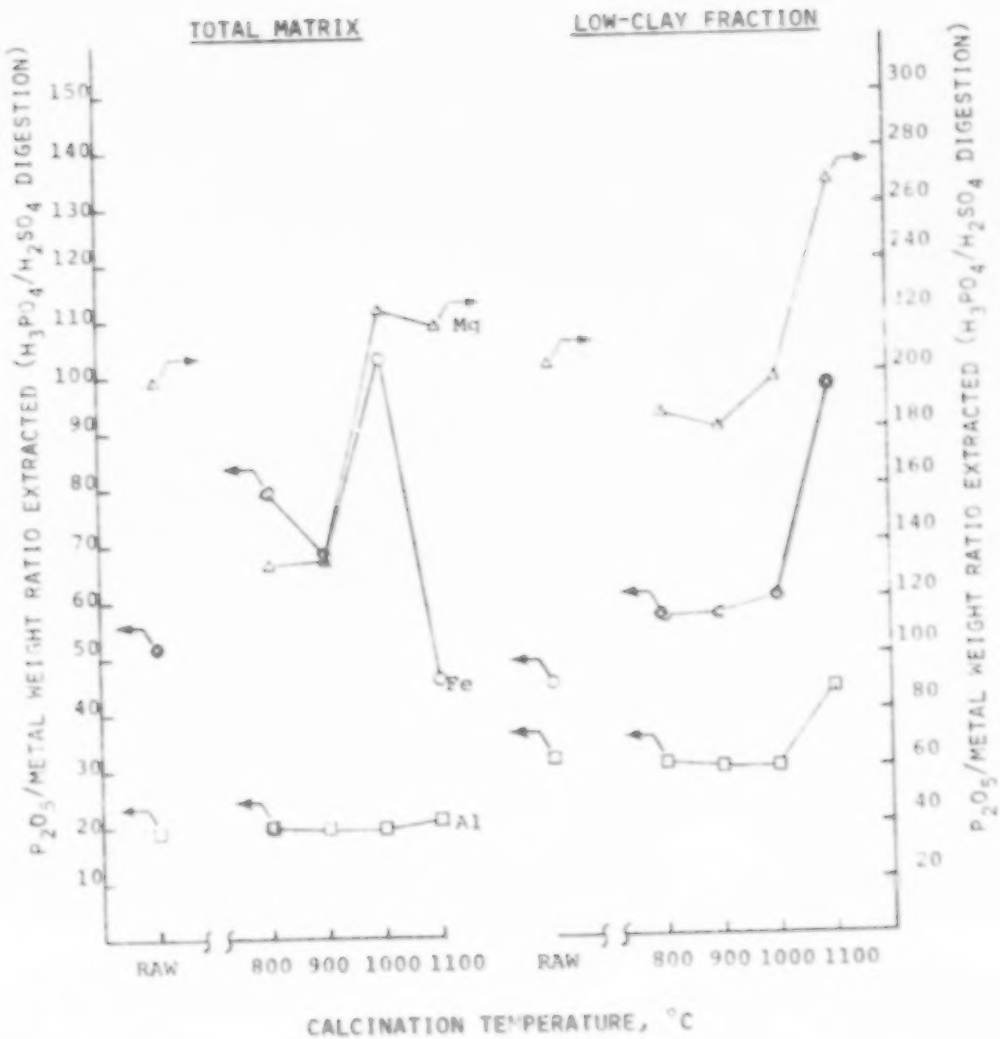


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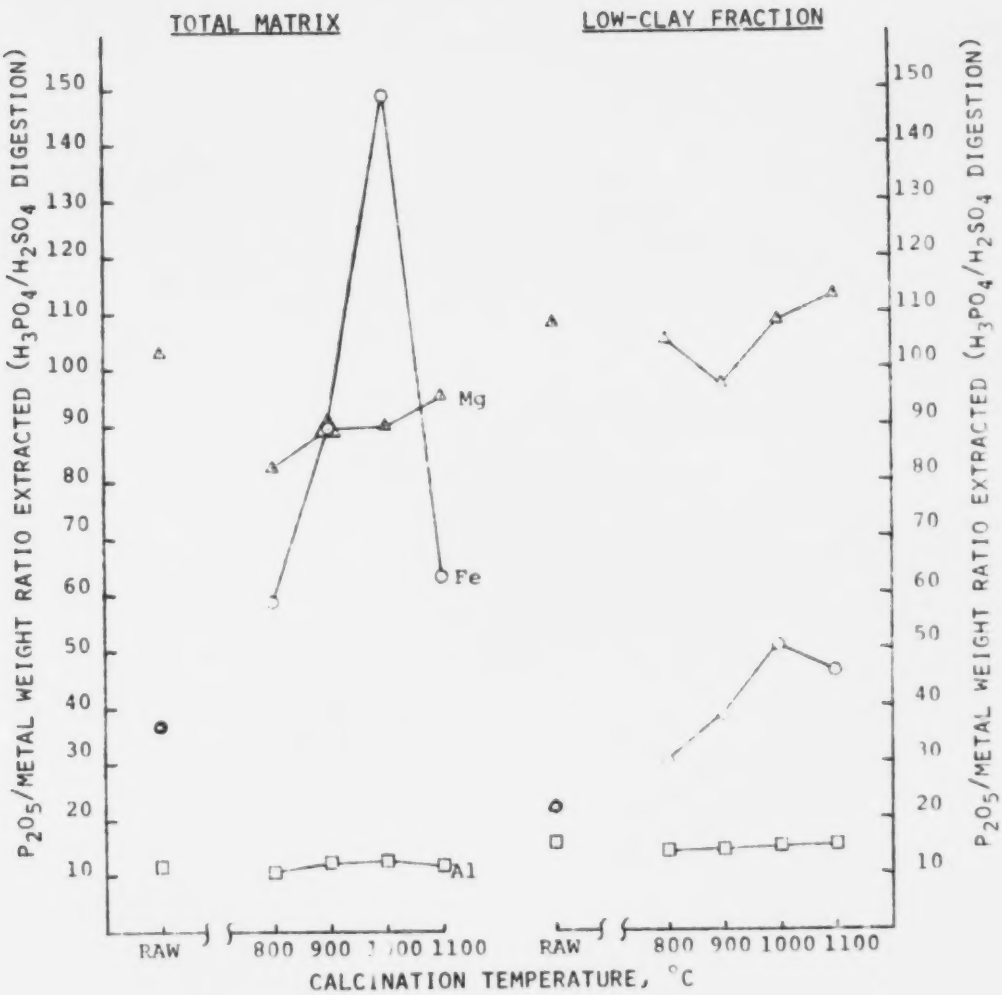
FIGURE 25

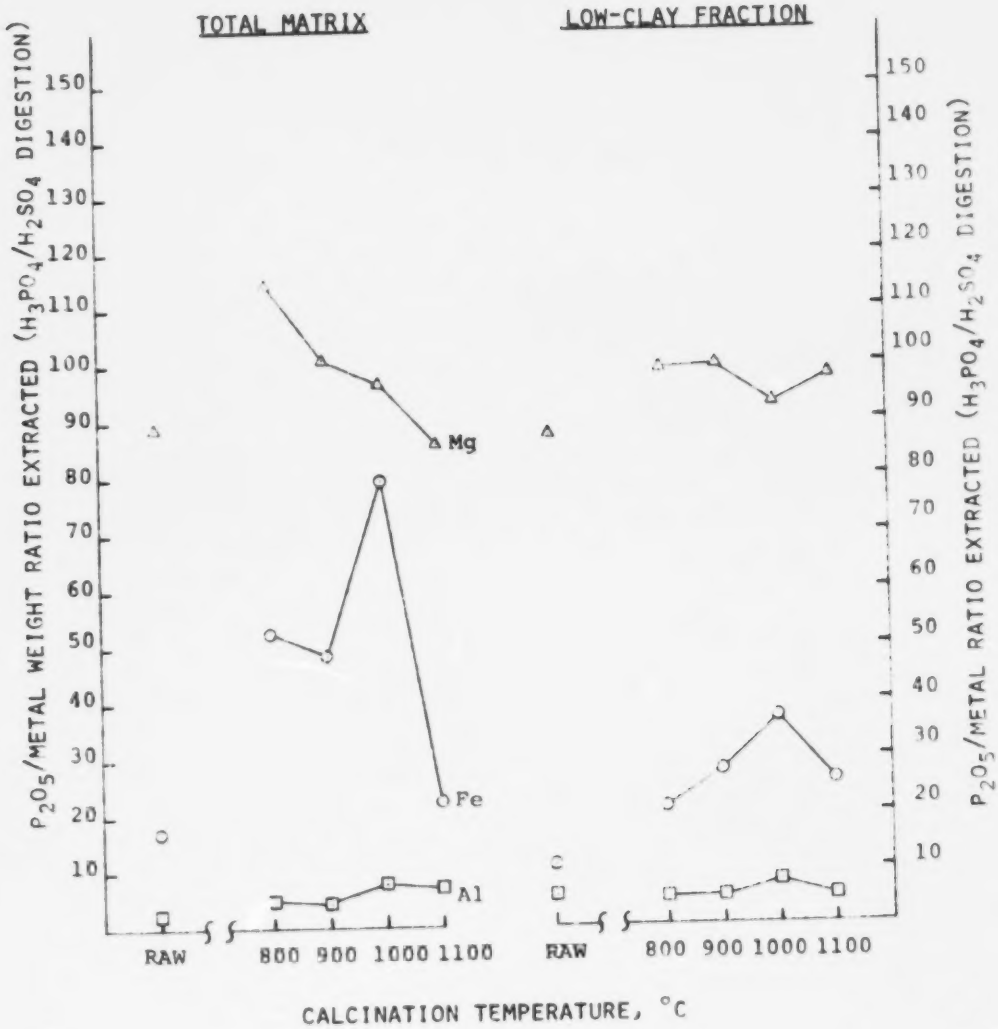
P_2O_5/METAL RATIOS OF
AMERICAN CYANAMID MATRIX



ATC 324-43

FIGURE 26

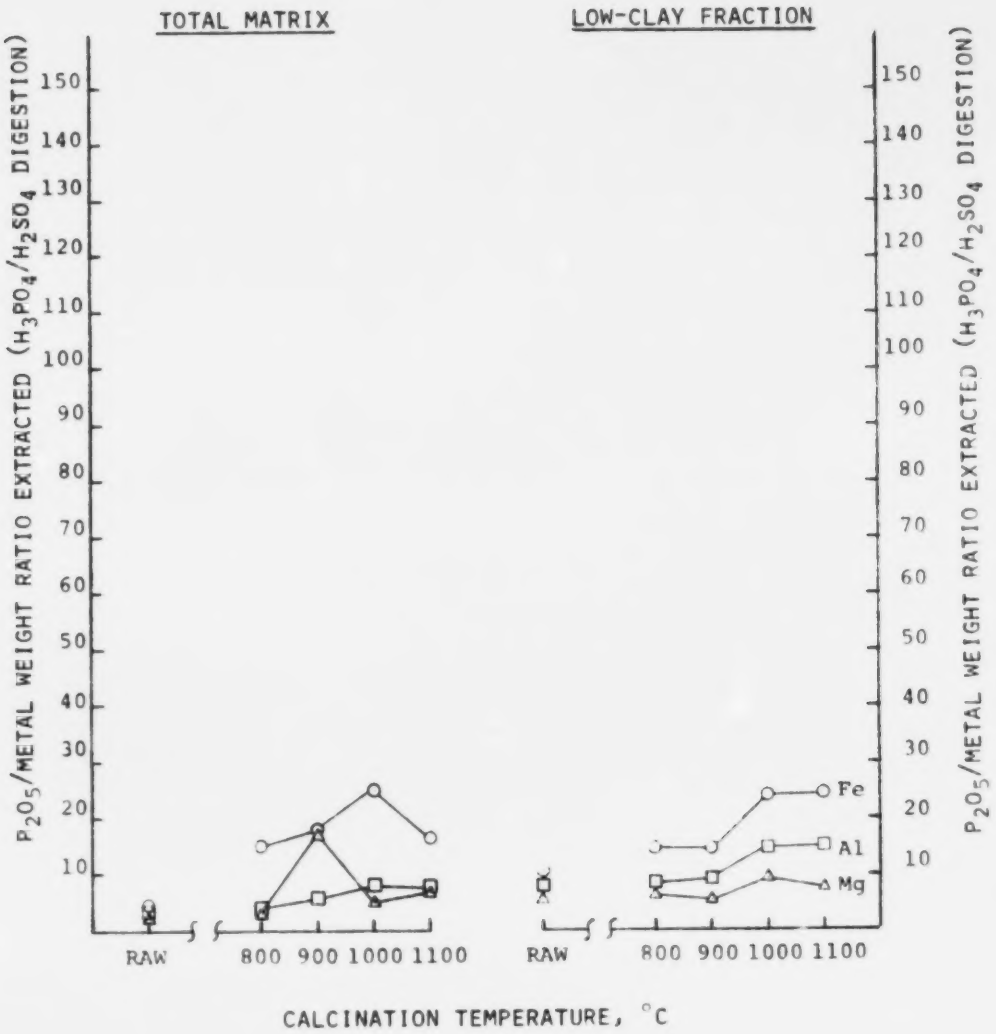
P_2O_5/METAL RATIOS OF
IMC MATRIX



ATC 324-46

FIGURE 27

P_2O_5/METAL RATIOS OF MOBIL MATRIX



ATC 324-48

APPENDIX C

LITERATURE SEARCH

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INTRODUCTION

This report contains the materials from a literature survey of Chemical Abstracts, covering Volumes 41-77 (1947-1972), for data relating to the EPA matrix process.

It was noted during the early stage of this work that very little information is available in the literature under the heading of "rock phosphate" which can be considered directly applicable to the proposed matrix process. Since, in general, Florida phosphate rock contains aluminum, iron, and magnesium minerals as the detrimental contaminants, these minerals, as well as many related materials listed below, were used as the key words in the reference scanning.

Actinolite ---------- $CaO \cdot 3(Mg,Fe)O \cdot 4SiO_2$
Aluminum Metaphosphate ---------- $Al(PO_3)_3$
Aluminum Oxide ---------- Al_2O_3
Aluminum Phosphates
Aluminum Silicates
Ankerite ---------- $2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$
Apatite ---------- $3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$
Apophyllite ---------- $K_2O \cdot 8CaO \cdot 16SiO_2 \cdot F \cdot 16H_2O$
Barbosalite ---------- $Fe(II)Fe(III)_2(PO_4)_2(OH)_2$
Ceramics
Corundum ---------- α-Al_2O_3
Crandallite ---------- $CaO \cdot Al_2O_3 \cdot P_2O_5 \cdot 6H_2O$
Cristobalite ---------- SiO_2
Dolomite ---------- $CaCO_3 \cdot MgCO_3$
Enamels
Feldspar (orthoclase) ---------- $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Goethite ---------- $Fe_2O_3 \cdot H_2O$
Illite ---------- K,Mg, Aluminosilicates
Iron Metaphosphates
Iron Oxides
Iron Phosphates

Iron Silicates

Kaolinite ---------- $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

Limonite ---------- $Fe_2O_3 \cdot 3H_2O$

Magnesite ---------- $MgCO_3$

Magnesium Oxide ---------- MgO

Magnesium Silicates

Millisite ---------- $2CaO \cdot Na_2O \cdot 3Al_2O_3 \cdot 4P_2O_5 \cdot 17H_2O$

Montmorillonite ---------- $(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$

Mullite ---------- $3Al_2O_3 \cdot 2SiO_2$

Phosphate Rock

Phosphoric Acid

Phosphorite

Staurolite ---------- $2FeO \cdot 5Al_2O_3 \cdot 4SiO_2 \cdot H_2O$

Tremolite ---------- $2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$

Turgite ---------- Hydrous Ferric Oxide

Vivianite ---------- $Fe_3(PO_4)_2 \cdot 8H_2O$

Wavellite ---------- $4AlPO_4 \cdot 2Al(OH)_3 \cdot 9H_2O$

Special attention was paid to their high-temperature chemistry, structural changes, formation of new phases, and changes in acid solubility of the metal impurities versus temperature of calcination.

Copies of abstracts from about 600 references were obtained initially, and 217 of them were selected for this report during the final screening. The selected abstracts were then edited, shortened, and grouped into a report form to meet our particular needs.

SUMMARY

Specific trends and results of the literature references are summarized in this section according to certain aspects which are of particular interest to the matrix process. Numbers in parentheses denote the reference as listed in the bibliography section.

1. Rock Phosphate, Apatite, and Tricalcium Phosphate

a. Fertilizer from High-Al Phosphate Ores

Leached-zone ore, containing about 15 P_2O_5, 1[illegible] Al_2O_3, 11 CaO, and 1.[illegible]% F was calcined at 1[illegible]-1150°C. and extracted with a mixture of 4[illegible]% HNO_3 and 5[illegible]% H_2SO_4 at 80-100°C. The filtrate contained about 90% of the P_2O_5 and [illegible]% of the Al_2O_3 originally present in the ore. The calcining step rendered a large proportion of the Al insoluble in the extracting acid (1). A Senegal ore, a mixture of crandallite and millisite, was calcined and ground, and the powder heated at 1000°C. for 2 hr. with petroleum coke under H_2 atmosphere. About 59% of the P_2O_5 was volatilized and 15% converted to ferrophosphorus. The β-$Ca_3(PO_4)_2$ present in the residue was completely recovered as H_3PO_4 with 2N H_2SO_4 (2).

b. High-Temperature Chemistry of Phosphate Rock

The calcination of Florida phosphate rock at 1000°C. caused considerable volatilization of F. However, the volatilization of Si with F was not observed. The growth of apatite crystals in the rock was remarkable, and the crystal quality of quartz accompanying the rock was lowered. The decomposition rate of phosphate by HCl was decreased (4). A phosphorite after heating to 300°C. contained $Ca_{10}(PO_4)_6 \cdot F_2$ 17.5, $Ca(PO_3)_2$ 26.5, $Mg(PO_3)_2$ 19.0, $Fe,Al(PO_3)_3$ 11.[illegible], $CaSO_4$ 15.9, $CaSiF_6$ 1.1, SiO_2 5.8 and $MgO + (Fe,Al)_2O_3$ 0.4%. Starting at 300°C., the formation of $Ca_3(PO_4)_2$ took place. At 300-700°C., compounds did not undergo structural changes, but at 800-900°C. their structural changes were considerable. After 900°C., $Ca_3(PO_4)_2$ remained stable.

Melting and further heating at [illegible]°C. lead to structural transformation (5).

c. Enrichment Processes for Calcined Phosphate Rock

Phosphate ore was thermally dried, while simultaneously subjected to attrition, air-classifying the dried ore to produce pebble phosphate and fine particles of phosphate rock, SiO_2, and agglomerated clay, and separating the pebble phosphate as a final product (6). Rock phosphate was partially disintegrated by calcination and H_2O-quenching. The disintegrated mass was made into a pulp and particles of finer size and lower density were stripped from the pulp by countercurrent washing. The concentrate that remained after washing was enriched in P_2O_5 [illegible].

d. Thermal Synthesis, Thermal Decomposition, and H_2SO_4 Decomposition of Apatite

Apatite was synthesized by heating a stoichiometric mixture of $CaHPO_4$, $CaCO_3$, and CaF_2 to 1000-1200°C. (9). The addition of catalytic amounts of SiO_2 to fluorapatite increased the volatility of F on heating in steam. $AlPO_4$, LiOH, and $CaCl_2$ decomposed apatite to form α-$Ca_3(PO_4)_2$, Li_3PO_4 and CaO, Ca_2PO_4Cl, or $Ca_{10}(PO_4)_6(Cl,F)_2$, respectively (10,11). The decomposition rate of apatite increased in dilute H_2SO_4 with increasing H^+ concentration, and reached a maximum at 5-[illegible] H_2SO_4, depending on temperature. Then, with increasing H_2SO_4 concentration, the rate decreased due to the formation of a gypsum coating, with a minimum at 60 and 50% H_2SO_4 at 25 and 90°C., respectively (13).

e. High-Temperature Chemistry of Tricalcium Phosphate

Tricalcium phosphate did not form a hydrate with a definite structure by the reaction of Ca salts with phosphate in aqueous solution, but formed a hydroxyapatite which was converted to β-$Ca_3(PO_4)_2$ at 700-800°C. Contrary to many other reports, β-$Ca_3(PO_4)_2$ was fairly soluble in citric acid. However, the solubility was reduced remarkably by a small amount of admixtures, expecially of MgO. The effect of Al_2O_3 and Fe_2O_3 was similar,

but not as intense as MgO (14, 15). The rate of H_2 reduction of $Ca_3(PO_4)_2$ was enhanced greatly in the presence of Al_2O_3. The equilibrium constants in the presence of SiO_2 and Al_2O_3 were $\sim 10^{-10}$ (at 1500°C.) and $\sim 10^{-10}$ (at 1300°C.), respectively (16). High-temperature phase equilibrium studies provided data for the systems $Ca_3(PO_4)_2$-Al_2O_3-SiO_2 (17) and CaO-MgO-P_2O_5 (18-20).

5. Clay Minerals and Clays

a. Dehydration and Lattice Changes on Heating

In the dehydration of Na and Ca montmorillonites, molecular water was essentially reversibly regained after mild heating, and partial dehydroxylation was followed by some reconstitution. Reconstitution of OH groups was about 60% around 300°C. and decreased to zero % at about 450°C. Interparticle water was "reversible" up to about 550°C. From about 500 to 800°C., all individual layers were inactivated by dehydroxylation (21-23). Li-saturated montmorillonite, however, exhibited pronounced irreversiblility of hydration after heating to 100°C. (24).

The isothermal decomposition of the clay minerals proceeded according to the first-order kinetics law. The activation energies for the Ca montmorillonite were lower than for Na montmorillonite, and closer to the value for the kaolinite (28).

The upper limits of temperatures (°C.) at which the breakdown of the colloidally dispersed minerals took place were montmorillonite 700, illite 450, kaolinite 500, hydrogoethite 350, halloysite 50, and metahalloysite 500 (29).

b. Preparation and Characterization of Clay Minerals

Montmorillonite was synthesized from SiO_2 gel, MgO, Fe_2O_3, Al_2O_3, KCl, and NaOH in 15 days at normal pressure, and temperatures up to 90°C. (30).

It was also synthesized from kaolinite and quartz by hydrothermal reaction with dolomite at [illegible]°C. [illegible]. Montmorillonite was formed from illite by the removal of K with Na cobaltinitrite or $MgCl_2$ [illegible].

Hydrothermal treatment of montmorillonite into which Al-OH polymers have been introduced readily generated kaolinite in quantity [illegible].

Montmorillonite lost its capacity of fixing and exchanging cations after prolonged grinding. A certain portion of the Al_2O_3, MgO, and all the [illegible] were liberated as grinding was continued. The Al_2O_3 and MgO thus liberated appeared to be able to recombine partially and form a new compound which was insoluble in acids [illegible].

Free oxides such as Al_2O_3, Fe_2O_3, and SiO_2 in montmorillonite can be determined based on the observation that when the sample is decomposed by an acid, a linear change of the internal surface area with the change in the amount of octahedral cations takes place [illegible].

The second endothermal DTA effect at [illegible]°C. in Na montmorillonite results from the dehydroxylation of the octahedral structural layer and from a partial dehydroxylation of the tetrahedral layers. The third endothermal DTA effect, at [illegible]°C., is related to the destruction of the crystal lattice and also with the final dehydroxylation [illegible].

The concentration of various montmorillonite types can be determined by X-ray from the relative 001 diffraction intensities of the glycerol complexes [illegible].

c. Acid Solubilities of Clays and Preheated Clays

Optimum conditions for the extraction of Al_2O_3 from uncalcined

and calcined clay minerals with acids, as stated in several references, are also included in this section. In our case, of course, we should try to avoid these conditions.

The Al atoms removed from montmorillonite crystals by hot acid treatment are in octahedral coordination with O atoms held by Si atoms. It is postulated that one of a pair of octahedrally coordinated Al atoms, together with two hydroxyl groups, are removed; this leaves the remaining Al atom in tetrahedral coordination (39).

In 5% HCl on exposure for 2 hr. at 80-85°C., the cation solubility (%) of montmorillonite was 62, kaolinite 10, biotite 100, muscovite 5-10, and halloysite 10-15. The solubility of montmorillonite depended more on the time of exposure than on HCl concentration. The solubility of aluminosilicate clay minerals in 25% HCl boiled for 2 min. was ≤10%, and the solubility of Fe-Mg silicate clay minerals was >10% (40).

HCl-insoluble residues of phosphate grains from the Atlantic Coastal Plain, the Pacific Ocean, and other areas consist largely of K feldspar and K mica in addition to quartz, organic matter, and Fe compounds (42).

Wavellite, crandallite, and millisite were completely dissolved by boiling 0.33-g. samples for 20 min. with 20 ml. 1:1 HCl. Only 1% of the Al present in kaolinite was dissolved. This method of decomposition is useful in differentiating the Al present in wavellite, crandallite, and millisite from that in kaolinite in samples from the Al phosphate zone of the Florida pebble phosphate deposits (43).

The reaction between montmorillonite and H_3PO_4 was rapid but incomplete. The reactions between kaolinite and H_3PO_4 and that between vermiculite and H_3PO_4 were slow but continuous. The reaction between chlorite and H_3PO_4 was rapid and complete (43).

A nonuniform transfer of Al, Fe, and Mg ions in solution was observed during the reaction of montmorillonite, kaolinite, and actinolite with 1 % H_2SO_4 solution. This was caused by changes in composition and structure of the solid phase. Replacement of bivalent Fe^{++} and Mg^{++} with H^+ occurred during the initial stage, and resulted in transfer of Fe^{++} and Mg^{++} into solution and hydration of the minerals (44).

On treating samples of montmorillonite, kaolinite, halloysite, pyrophyllite, and zeolite with boiling solutions of 5-30% H_2SO_4, the major change was the removal of Al_2O_3 from montmorillonite and halloysite. IR absorption spectra show that the O-H bands near 3700 cm.$^{-1}$ and 950 cm.$^{-1}$ weakened as Al_2O_3 was removed; the Si-O band in the 1000-1200 cm.$^{-1}$ region changed from V- to U-shape (45).

Kaolinitic clay and hydromicaceous clay specimens, after calcination in the 500-800°C. range for 1 hr., yielded 100 and 57% of their Al_2O_3 contents, respectively, on extraction with 5% HCl. From a montmorillonite clay processed under the same conditions, only an insignificant amount of Al_2O_3 was extracted. This is because the Al hydrosilicate of the montmorillonite is surrounded by two layers of silicic acid in its 3-layer crystal lattice; in the case of kaolinite clays, the 2-layer lattice consists of alternate layers of alumina and silicic acid (46).

The ratio of dissolved SiO_2 to Al_2O_3 in boiling HCl (0.1 to 10.5N, 60 min.) seemed to be a constant for the same type of clay. The absolute value of the dissolved material is a measure of the amorphous material contained in the clay. If the sample was first preheated to 750°C., the solubility of Fe_2O_3 in HCl increased, whereas the solubility of SiO_2 and Al_2O_3 did not change (59).

A process for the extraction of Al_2O_3 from clay with HNO_3 involved calcining the ore at 750°C., followed by digestion at 165°C. and 85 psig. with 30% HNO_3 (60).

The optimum conditions for the production of Al_2O_3 from Egyptian kaolin are: Grinding to 60 mesh, calcining at 750°C. for 1 hr., and boiling for 1 hr. with 40% H_2SO_4, 20% HCl, or 32% HNO_3. The yields amount to 84, 81.5, and 78%, respectively (61-63).

The exothermic reaction of kaolinite begins at 800°C. This is related to the extraction of Al_2O_3 from kaolinite by HCl, which attains its maximum recovery when the material is preheated to 750-800°C. This phenomenon may be attributed to an increasing disorder of the lattice (64).

In an attempt to extract Al_2O_3 from kaolinite with H_2SO_4, unroasted ore produced only 38% yield. The maximum yield (98%) was obtained by heating the ore to 650-750°C. for 1 hr. prior to the acid extraction. Higher and longer duration lowered the yield because of spinel, $Si_3Al_4O_{12}$, formation (65,66).

The rate of Al_2O_3 leaching from a calcined kaolin sample was most rapid with HCl, slower with H_2SO_4, and slowest with HNO_3. The acid concentrations used were 5.9 and 8.6N, with reaction temperatures of 95, 80, and 60°C. (67).

By using a melting-quenching-H_2SO_4 leaching scheme, over 95% of the Al_2O_3 was extracted from various silicates containing 30-45% Al_2O_3. The optimum conditions consisted of quenching the melted material to a completely amorphous state and adjusting the weight ratio of $SiO_2/(CaO+Na_2O)$ in the quenched product to 3.0-3.7. At higher ratios, recovery of Al_2O_3 decreased (68,69).

The steep increase in Al_2O_3 solubility in acid after preheating

a kaolinite clay specimen at 400-500°C. is explained by the breakdown of the structure due to water release. This gives a more open structure with easy access for the acid (70).

Preheating at 1000°C. did not increase the corrosion resistance of halloysite as much as kaolinite in acids. Solubilities of Al_2O_3 and Fe_2O_3 were 20-30 and 50-70%, respectively, for the preheated halloysite. After preheating at lower temperatures (≤400°C.), an even higher solubility of both Al_2O_3 (≤40%) and Fe_2O_3 (>90%) was obtained. The maximum solubility (~100%) was obtained for a preheating temperature between 600 and 800°C. The cause of the generally low corrosion resistance of halloysite are (a) higher stacking-fault disorders, (b) wide interlayer gaps because of the additional interlayer H_2O, and (c) incomplete structural changes during the short-duration heat treatment at 1000°C. The last point was verified by heating halloysite for 15 hr. at 1000°C., which lead to only 1% solubility of Al_2O_3 in acid (71).

The firing of clay proceeded in two stages, during which the properties of SiO_2, Al_2O_3, and alkali metal oxide compounds were changed. In the first stage, decomposition of clayey minerals occurred, accompanied by an increase in the solubility of compounds in acid and in alkalies. In the second stage, formation of new phases occurred, which was associated with a decrease in the solubility of new compounds. In a reducing atmosphere, both stages began at lower temperatures. When firing clay at temperatures above 900°C. in an H_2 current, the solubility of compounds of Al_2O_3, K_2O, Li_2O, and others in 5% HCl increased anew. This increase is explained by the conversion of newly formed compounds into other compounds which are more soluble in HCl. In an H_2 current at 600°C., and in an air current at 700°C., carbonates contained clay decomposed in 2 stages. Free MgO was liberated in the first stage, and free CaO in the second stage (72).

Ceramics prepared from kaolinite-hydromiceous clay at 1000°C. consisted of quartz, small amounts of mullite, and an amorphous phase. They showed a low volume weight and a low acid resistance. At 1000-1100°C., the content of mullite rose, while the content of amorphous phase and quartz decreased somewhat. The mechanical strength, volume weight, and acid resistance of samples rose between 1100-1200°C. In this interval, the growth of mullite crystals commences. Above 1200°C., all properties studied increased only slightly. The ceramics prepared from kaolinite-montmorillonite clay at 1000°C. consisted of cristobalite and mullite. The cristobalite content increased sharply at 1050-1100°C. The ceramics prepared from kaolinite clays, at temperatures up to 1100°C., consisted of amorphous products of the decomposition of clayey mineral and quartz. The strong crystallization of mullite and cristobalite, causing increase of acid resistance, starts at 1100-1200°C. At 1300°C., the content of amorphous phases is practically zero. The acid resistance of materials depends not only on the phase composition, but also on the amount of succession of formation of phases (73).

d. High-Temperature Chemistry of Clay Minerals

After deterioration of the lattice of montmorillonite at 900°C., amorphous SiO_2, quartz, and some spinel were found; at 1000°C., cristobalite, more quartz, spinel, anorthite, and less amorphous SiO_2; at 1100°C., more cristobalite, anorthite, spinel, less quartz, and appearance of cordierite and mullite; at 1200°C., more mullite, anorthite, cordierite, and spinel (48-54).

Gradual formation of Ca silicates occurred on prolonged heating of clays with $CaCO_3$. Feldspar formed on heating clays with KCl or $CaCl_2$, but NaCl and Na_2SO_4 gave sodalite and noselite, respectively. Addition of NaCl or KCl caused the beginning formation of mullite at 850°C., which otherwise begins only above 1000°C. (55).

The high-temperature crystal phases which develop on heating of clay minerals are related both to structural inheritance and to composition. Minor chemical variations and the presence of trace impurities play a large role in phase development of 3-layer clay minerals. Nonclay components, such as feldspar and mica, often react to alter the predicated firing response of specific clay minerals in the mix. Alkali elements and Fe are particularly effective in reducing phase minerals development (56).

The dehydrated kaolinite is purely amorphous in character, and the exothermic reaction, which occurs at 980-1000°C., is the sudden crystallization of γ-Al_2O_3 from the amorphous phase, which is prevented at low temperature by the SiO_2 in intimate contact with it (74, 75). The dehydration at 500-600°C. destroys the octahedral layers and distorts the tetrahedral layers. One half of the Al^{3+} ions migrate to the previous position of the lost OH groups (empty positions in the tetrahedral layers). At 850-900°C., the atoms of the residual octahedral layers are regrouped to form γ-Al_2O_3 (76). Fe, Mg, and Ca impurities influence both the chemical and the phase changes. In the first exothermic range, 920-1000°C., either γ-Al_2O_3 or mullite forms, depending on the impurities present. This influences the rate of sintering and the origination of a second exothermic range, 1150-1300°C., corresponding to the formation of mullite (77-88). The mineralogical sequences observed during the firing of impure clays are as follows (89-93):

$$\text{Kaolinite} \xrightarrow{<500^\circ\text{C.}} \text{Metakaolinite} \xrightarrow{750\text{-}920^\circ\text{C.}} \text{Al-Si Spinel and } SiO_2 \xrightarrow{870\text{-}1040^\circ\text{C.}} \text{Mullite and Cristobalite.}$$

The solid-phase conversion of kaolinite to mullite follows a first-order equation relative to the unreacted part in the initial stages of the process. The mullite in the quickly cooled specimens is more soluble in aqueous HF than in the slowly cooled

specimens (94). Mullite formation from kaolinite-type minerals is affected by the firing atmosphere. The reaction is greatly enhanced by H_2O vapor and vacuum, and to a lesser extent by N_2 and H_2, but is retarded by O_2 and CO_2. The crystallization reaction of cristobalite from amorphous SiO_2 is enhanced by N_2, CO_2, H_2O, and vacuum, rather unaffected by O_2 and air, and retarded by H_2 (95, 96). In the presence of a solid reducing agent such as carbon, the rate increases. Thus, if under normal conditions mullite crystallizes at 1250°C. or above, the presence of carbon brings crystallization at or below 1200°C. (97).

In the sintering of kaolinite, the amount of mullite formed at 1200°C. increases with increasing Fe_2O_3 content. At higher temperatures, it decreases if the Fe_2O_3 content exceeds 7.7% (98, 99). FeO also has a favorable effect on mullite formation from kaolinite; it decreases the reaction temperature by 150-200°C. In the kaolin-FeO system, hercynite forms first on heating, and contributes to the decomposition of metakaolin to quartz, mullite, and amorphous SiO_2. Fayalite is formed only when the Fe_2O_3 content is high (100).

High-temperature reaction studies on kaolinite-feldspar-quartz mixtures indicate the amount of quartz in the fired materials decreases with increasing temperature and increasing feldspar content. No feldspar is unreacted in mixtures fired at 1200°C. or above. Mullite develops very rapidly in the mixtures as the temperature rises from 1100 to 1200°C. The amount of mullite developed at 1200°C. is only slightly less than that found at 1300-1400°C. The main hindrance to attainment of full equilibrium at 1200°C. and above is the slow rate of dissolution or reaction of the quartz (101-103).

e. Effect of Mineralizers on Mullite Formation

References which have some immediate bearing in our experimental

work are the use of additives in the high-temperature conversion of clay minerals to mullite. Very effective additives mentioned include C, H_2O(vapor), FeO, MnO, NaCl, KCl, LiF, $NH_4F \cdot HF$, CaF_2, AlF_3 and Na_2SiF_6. These additives, in general, either promote mullite formation or lower the temperature required for mullite formation, or both. In most cases, the amount of mullite formed when small amounts of additive are used is greater than in the case without additives. If the proportion of the additive exceeds the usually small optimum amount, however, mullite formation is reduced and eventually is less than in the control sample. In addition, there exists an optimum temperature and an optimum time of calcination with a given additive.

The phase transformations that occur in montmorillonite, illite, kaolinite, and halloysite at temperatures up to 1450°C. were investigated. Continuous high-temperature XRD is used to detect changes that take place in the firing history of a clay in which small amounts of chemical impurities or other mineralizing substances are present or have been added. Several chemical impurities were added to each of the clays to determine their ability to either enhance or retard structural transition and new mineral development upon firing. The effects which these additives have on predicted structural changes are illustrated and are interpreted in lieu of chemical and structural requirements (105).

Clays heated for 3 hr. at 1100, 1200, and 1500°C. showed 31, 38, and 47% mullite, while the theoretically possible maximum yield is 49-59%. With the addition of 4% of $MnSO_4$, $MgCl_2$, or $CuCl_2$, the temperature of the beginning of mullite formation was lowered by 100-200°C. (107).

Mullite formation was accelerated by the addition of mineralizers, the most effective being CaF_2 (108). The temperature of mullite formation was reduced from 1300 to 600°C. by the addition of 5-20% AlF_3 (or $AlCl_3$) to the Al_2O_3-SiO_2 or clay-Al_2O_3 mixes. At 1000°C., the product was more compact with better mechanical

strength, and was better crystallized (109). Mullite can be formed in kaolin at temperatures considerably lower than normal by introducing small amounts of fluorides (Na_2SiF_6, $NH_4F \cdot HF$, BaF_2, AlF_3, SbF_3). The dissolution rate of kaolin in molten fluorides is very high. Very little F is detectable in the fired kaolin. The mullite which forms is identical to the mullite that is conventionally formed in kaolin at 1200°C. (110). Alkali and alkaline-earth fluorides promote the formation of mullite from kaolin minerals, LiF being the most effective. The dried materials were mixed with 2.5, 5, and 10% LiF and heated for 5 hr. at various temperatures. Mullite started to form at 800°C. with 2.5% LiF added to the kaolin, at 700°C. with 5% LiF, and at 500°C. with 10% LiF (111-113).

Generally, the greater the ionic charge and the smaller the ionic radius, the more active is the ion in its mineralizing effect. CaF_2 is more active than $CaCO_3$, while LiF is more active than LiCl. In most cases, the amount of mullite formed when small amounts of mineralizer are added is greater than in the original mixture without any additions. If the proportion of the mineralizer is increased above some quite-small optimum amount, however, mullite formation is reduced and eventually is less than in the original mixture. In addition, there exists an optimum temperature and an optimum time of calcination with a given mineralizer (114-117).

If 2% Fe_2O_3 was added to kaolin, the crystallization of γ-Al_2O_3 was considerably accelerated at 930°C., but mullite appeared only in the range from 1160 to 1360°C. Three % of MgO, CaO, CaF_2, MgF_2 added to kaolin increased the effect at 930°C. and reduced the exothermic reactions at 1050 to 1140°C. The natural contaminations of kaolins and clays by Fe_2O_3, MgO, CaO, etc., have important effects on the mullite formation in ceramic bodies (118). The addition of FeO to kaolin up to 10% at 900-1500°C. effected the phase composition, mullitization, and morphology of mullite (119). The activity of mineralizers such

as K_2O, MgO, CaO, TiO_2, Fe_2O_3, MnO, PbO, and P_2O_5 increased with an increase in SiO_2 content, while their influence decreased with an increase in firing temperature (120). Among the oxides Na_2O, K_2O, MgO, CaO, CuO, Al_2O_3, Fe_2O_3, TiO_2, and P_2O_5 best sintering additive was MgO. The use of combined R_mO_n + P_2O_5 additions gave better results in kaolin sintering than if either P_2O_5 or R_mO_n were used alone. The open porosity of fireclay products without additions of oxides was about 1.4-2.9 times as high as that of products with additions, or the same porosity results at firing temperature of about 100-150°C. lower (121). The additions of Na_2O, K_2O, MgO, or CaO accelerated thermal transformations of pyrophyllite, the most effective being K_2O. In the mineral containing K_2O, mullite was detected in samples ignited at 900°C. (122). The formation of mullite from mixtures of 3:2 Al_2O_3-SiO_2 with different amounts of NaF, B_2O_3, Fe_2O_3, or TiO_2 at 1400-1600°C. is related to the capacity of these mineralizers in the mullite cell and to the liquid phase formation of the system. The formation of substitutional solid solutions with Fe_2O_3 and with TiO_2 promoted formation of mullite (123).

3. Aluminum Phosphate Minerals and Aluminum Phosphates

a. Synthesis of crandallite, variscite, and wavellite (125).
b. XRD and DTA data of crandallite, millisite, and wavellite (126-129).
c. Preparation of ammonium phosphate fertilizer from Al-phosphate ores and NH_4F (130).
d. Preparation of phosphorus from Al-phosphate ores (131).
e. Reaction of H_3PO_4 with some forms of Al_2O_3 (132).
f. System Al_2O_3-P_2O_5-H_2O at 25-90°C. (133-136).
g. System Al_2O_3-P_2O_5-SiO_2 (137-139).
h. XRD and DTA data of $AlPO_4$ (140-143).
i. IR spectra of $AlPO_4 \cdot 2H_2O$ (144).
j. High-temperature chemistry of Al phosphates (145-155).

4. Aluminum Silicate Minerals and Aluminum Silicates

a. Composition, structure, and properties of staurolite (156-159).
b. Recovery of Al_2O_3 from staurolite concentrates (160).
c. Growth of mullite crystals in feldspathic glass (161, 162).
d. Analyses and properties of feldspars (162-166).
e. High-temperature reactions between mullite and Na_2O, K_2O, MgO, CaO, Fe_2O_3, or TiO_2 (167-170).
f. Phase transformations in Al_2O_3-SiO_2 mixtures (171-174).
g. Phase equilibrium for the system Al_2O_3-SiO_2 (175-178).
h. Stability of silicate materials in H_2SO_4, H_3PO_4, and HCl (179-180).

5. Aluminum Oxide

a. Phase transformations of Al_2O_3 (183).
b. Corrosion resistance of hydrous Al_2O_3 (182).
c. Corrosion resistance of Al_2O_3-base materials versus HCl, HNO_3, and H_2SO_4 (181).

6. Iron Oxide Minerals and Iron Oxides

a. Leaching of Goethite with H_2SO_4, HCl, $HClO_4$, or Mixtures of these Three Acids.

A first-order dependence of leaching rate on H^+ activity was observed. The grain-to-particle-size ratio of the oxide being leached determined the shape of the leaching curve (185, 186). In 1:1 H_3PO_4 at 100°C., only 10-20% of the Fe in goethites was soluble, while the limonites dissolved almost completely, with the hydrogoethites taking an intermediate position (187). The dehydration of limonite went through the stages: Amorphous $Fe(OH)_3$, hydrogoethite, goethite, and hydrohematite (188).

b. The Dissolution Rate of Fe_2O_3 in H_2SO_4 Decreased with the Degree of Crystallinity (189).

The times required for 100 mg. Fe, in the form of Fe_2O_3, to

dissolve completely at 60°C. were 28 hr. in 6.1% H_2SO_4, 16 hr. in 4.6% HCl, and 0.36 hr. in 2.5% HF. The corrosive effect of acids was accelerated by the addition of HF (190). The dissolution of Fe oxides at 60°C. and at the boiling points in H_2SO_4 was about 30% slower than in HCl. The addition of 5mM HF to 0.5M HCl increased the dissolution rate of Fe_3O_4 by a factor of 10, the addition of 20 mM HF by a factor of 100 (191).

7. Iron Phosphate Minerals and Iron Phosphates

a. Thermal decomposition of vivianite and its stability in the system $Fe_3(PO_4)_2$-H_3PO_4-H_2O (196,197).

b. Reactions in the Fe_2O_3-$FePO_4$ system (198,199).

c. Phase equilibria in the system Fe_2O_3-H_3PO_4-H_2O at 25°C. (200, 201).

8. Magnesium Carbonate Minerals and Magnesium Oxide

a. Thermal Decomposition of Magnesite, Dolomite, and Ankerite

At 400-600°C., small MgO particles were formed by the decomposition of $MgCO_3$. Between 600 and 800°C., these particles grew into large, porous secondary aggregates, and the porosity of the unchanged $MgCO_3$ particles also increased. Sintering began at 850°C., with greater adherence of the particles to each other, and decreasing aggregation and porosity. Sintering was completed at 1050°C., and sharply defined cubic crystals of MgO were observed in large numbers. With natural magnesites containing traces of Fe and Al oxides, the decomposition began at higher temperatures than in pure $MgCO_3$, and the recrystallization process also began at higher temperatures (202). The type of process used for calcining magnesite and dolomite significantly affects the recrystallization rate of MgO. Calcination at 800-1250°C. in shaft and rotating kilns resulted in the growth of MgO and CaO crystals. During the short-term firing of fine fractions in a fluidized bed at 900-950°C., lime was obtained

in which the MgO was converted into the active form (204).

Dissociation products, MgO and calcite, appeared after the dolomite was heated to 400-500°C. After calcining at 700°C., the dolomite crystals acquired a trizonal (unaltered dolomite, MgO and calcite, calcite) structure. After calcining at 800°C., no unaltered dolomite remained. In the 1000-1100°C. range, MgO recrystallized as periclase. MgO did not react with unground silica sand, but reacted vigorously with ground sand, forming Mg hydrated silicates, similar to serpentine in composition (205, 206).

Alkali salts affect the decomposition of dolomite at the first stage only. The decomposition temperature is lowered by about 150°C., which affects the MgO content, crystallite growth, surface area, and porosity, leading to a higher reactivity of the products. At higher temperatures, the additives decrease the reactivity due to the lattice diffusion leading to the structure ordering and the removal of defects (210). The presence of CaF_2 increases the decomposition rate of magnesites and dolomite. The activity of ignited materials depends on the temperature of ignition and on the character and distribution of admixtures (Fe_2O_3, Al_2O_3, SiO_2) or special additions (CaF_2). The higher the ignition temperature and/or the higher the concentration of admixtures or additions, the lower the reactivity of the product (212).

On heating a powdered ankerite sample at 600°C. for 6 hr., no change in the X-ray powder pattern occurred. The 750°C. pattern indicated a mixture of calcite with small amounts of MgO and vaterite. At 950°C., a mixture of $Ca_2Fe_2O_5$, MgO, and CaO was formed (214). Ankerite was not only thermally dissociated into CO_2 and oxides, but also formed $MgFe_2O_4$. It arose in the presence of Ca^{2+} in a narrow temperature range near 700°C. At higher temperatures it was transformed to $CaFe_2O_4$ (215).

b. Dissolution of Calcite, Dolomite, and Magnesite in Acids

Magnesite and dolomite dissolved to a considerable extent in 0.1N solutions of HCl, H_2SO_4, HNO_3, or H_3PO_4 after 10 min. in the cold, and almost completely after 40 min. Calcite in the cold in 0.1N HCl dissolved completely within 1 min. (216).

c. Reaction of Dolomite with $(NH_4)_2SO_4$ Solution

$CaSO_4$ was formed faster from dolomites calcined at 1000°C., while $MgSO_4$ formation was faster from dolomites calcined at 850°C. (217, 218).

d. Sintering and the Rate of Hydration of MgO

CaO inhibits sintering to an extent that appears limited by particle contact. TiO_2 promotes sintering as well as growth of the periclase crystals. However, there is an optimum concentration of TiO_2, SiO_2, and Al_2O_3 beyond which sintering is inhibited. The rate of hydration is controlled by the % of open pores and crystal size of the periclase (219-221). Water vapor pressure (10^{-3} to 5 mm. Hg) profoundly affects the nature of thermal decomposition products such as MgO, CaO, and BeO in relation to the crystal size and pore structure. On subsequent sintering of the oxides, similar H_2O vapor pressures may increase the rate of crystal growth by >2 orders of magnitude (221, 222).

e. Infrared Absorption Spectra of Metal Oxides

The IR absorption spectra of 25 metal oxides such as Al, Fe, Mg, Ca oxides, and silica over the range 1400-400 $cm.^{-1}$ are given (223).

9. Magnesium Silicate Minerals

Information on high-temperature chemistry of actinolite, anthopylite,

deweylite, forsterite, saponite, sepiolite, and tremolite are given (225-228).

10. Magnesium Phosphates

a. Phase equilibria in the system $MgO-P_2O_5-H_2O$ at 0 to 150°C. (229, 230).

b. Interaction of MgO with H_3PO_4 (231).

c. Thermal decomposition of $Mg(H_2PO_4)_2 \cdot 2H_2O$ (232).

11. Binary and Ternary Systems of Al_2O_3, Fe_2O_3, MgO, and SiO_2

a. The formation and subsequent decomposition of the spinel ($FeO \cdot Al_2O_3 + CO \longrightarrow Fe + Al_2O_3 + CO_2$) occurred during the reduction of Fe_2O_3 by CO in the presence of Al_2O_3 (233). Binary compounds of the alum type, $M_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot nH_2O$, resulted from the sulfatization of Al_2O_3 and Fe_2O_3 with $(NH_4)_2SO_4$ at 300-400°C. (235). When powder mixtures of M_2O_3 and Na_2SiF_6 were heated to 700-800°C., the reaction $6Na_2SiF_6 + 2M_2O_3 \longrightarrow 4MF_3 + 12NaF + 3SiF_4 + 3SiO_2$ reached the maximum rapidly with Fe_2O_3, and after 45-60 min. with Al_2O_3 (236).

b. When mixtures of Al_2O_3 and MgO were heated to between 800 and 1200°C., pure $MgAl_2O_4$ was formed at first, and the solid solution rich in Al_2O_3 was formed gradually when an excess of Al_2O_3 was present (237, 238). Spinel was produced by treating compacted Al_2O_3 with MgO as the vapor carried by H_2, or as a MgO compound such as carbonate. The reaction was promoted by heating at 1500-1900°C. (241). A solid-solid reaction mechanism is suggested, based on initial formation of spinel at the contact surface, followed by dissolution of Al_2O_3 in the spinel and by its penetration into it, to react further with MgO to form more spinel (243). With the presence of $MgCl_2$, MgO dissolved in molten $MgCl_2$ spread uniformly over the surface of Al_2O_3 particles, then MgO was transported to the inner part of

Al_2O_3 particles and rapidly reacted with Al_2O_3 to form the spinel layer through which the counter diffusion of Mg^{2+} and Al^{3+} occurred (244).

c. The reaction $MgO + Fe_2O_3 \longrightarrow MgFe_2O_4$ occurred when a mixture of MgO and Fe_2O_3 was heated at 850-1000°C.(247-249). The solubility of MgO in HCl was the highest when it was prepared by firing $Mg(OH)_2$ at 300°C. For $MgFe_2O_4$, MgO was preferentially solubilized at the initial stage (251).

d. During the reduction of Fe_2O_3 by CO in the presence of SiO_2, the new solid phases that appeared successively were magnetite, fayalite, and metallic Fe (252). When Fe_2O_3 and SiO_2 were heated in O_2, a light-red solid solution of Fe_2O_3 in cristobalite was obtained above 900°C.(253).

e. The ternary system Al_2O_3-Fe_2O_3-SiO_2 was determined by the phases appearing in the adjacent systems. A ternary combination of oxides could not be observed (254).

f. A critical review and discussion on the phase diagram of Al_2O_3-MgO-SiO_2 is given (255, 256). Metastable solid solutions of quartz structure along the composition line $MgAl_2O_4$-SiO_2 in the range 41.5-73.2% SiO_2 were obtained (257). Mixtures along the mullite-spinel line of the Al_2O_3-MgO-SiO_2 system were synthesized by firing the component oxides. At 900°C., highly defective fine crystalline spinel was formed. At 1200-1300°C., sapphirine and cordierite appeared, and subsequently decomposed into spinel, mullite, and a liquid phase. Above 1550°C., mullite decomposed into corundum and a liquid. Sintering compressed mixtures for 15-30 min. at 1550-1630°C. gave refractories stable in boiling concentrated HCl and H_2SO_4 (259, 260).

12. Acid-Resistant Ceramics, Cements, and Enamels

One noteworthy reference (263) remarked that ceramics containing anorthite gave good resistance to concentrated H_2SO_4.

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